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THE CRYSTALLIZATION CONJECTURE: A REVIEW

XAVIER BLANC AND MATHIEU LEWIN

ABSTRACT. In this article we describe the *crystallization conjecture*. The latter intends to investigate why interacting particles often place themselves into periodic configurations, breaking thereby the natural translation-invariance of the system. This famous problem is still largely open. Mathematically, it amounts to studying the minima of a real-valued function defined on \mathbb{R}^{3N} where N is the number of particles, which tends to infinity. We review the existing literature and mention several related open problems, of which many have not been thoroughly studied.

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1. INTRODUCTION

At the microscopic scale, most crystals are composed of atoms which are arranged on a periodic lattice. This specific geometric structure has important consequences at the macroscopic scale. For instance, in snowflakes the atoms are arranged on an hexagonal lattice, which explains the beautiful six-pointed figures that can be found in nature. The aim of crystallography is to study those periodic structures and their properties at larger scales.

2014 was declared the year of crystallography by UNESCO [172] and this gives us the opportunity to draw attention to a difficult mathematical conjecture, also important from a physical point of view, which has been studied a lot without being completely solved. If crystallographers study the properties of some periodic arrangements and compare them, a more fundamental question can be raised: why is it favourable (at low temperature) for the atoms to spontaneously arrange themselves on a periodic array? This periodic order seems to only appear in the limit of a large number of particles, which makes the question particularly difficult.

In this article we rigorously formulate the above question and we make a review of the existing results as well as of the remaining open questions. We will mostly discuss the simplest model

(classical particles interacting with a two-body potential at zero temperature), before addressing more advanced situations (for instance quantum systems).

2. THE CLASSICAL MODEL

2.1. Energy. Let us consider a set of N classical identical particles in \mathbb{R}^d (in practice $d = 1, 2, 3$), interacting by pairs through a potential V depending only on the distance between them. We denote by $x_1, \dots, x_N \in \mathbb{R}^d$ and $p_1, \dots, p_N \in \mathbb{R}^d$ the positions and momenta of these particles. The model to be used is that of the Hamiltonian dynamics, based on the energy

$$\mathcal{H}_N(x_1, \dots, x_N, p_1, \dots, p_N) = \sum_{i=1}^N \frac{|p_i|^2}{2m} + \sum_{1 \leq i < j \leq N} V(|x_i - x_j|). \quad (1)$$

Here m is the mass of the particles and $|\cdot|$ is the Euclidean norm of \mathbb{R}^d .

At zero temperature, the equilibrium states are the minima of \mathcal{H}_N , which all satisfy $p_1 = \dots = p_N = 0$. If one is only interested in those, it is therefore sufficient to consider the potential energy

$$\mathcal{E}_N(x_1, \dots, x_N) = \sum_{1 \leq i < j \leq N} V(|x_i - x_j|),$$

and to understand how the x_i 's solving the minimization problem

$$E(N) = \inf \left\{ \mathcal{E}_N(x_1, \dots, x_N), \quad x_1, \dots, x_N \in \mathbb{R}^d \right\}, \quad (2)$$

are arranged in \mathbb{R}^d in the limit $N \rightarrow +\infty$. Let us note that \mathcal{E}_N is invariant under translations. Any configuration may be translated by a fixed vector without changing the total energy. Minimizers of (2) are thus not unique. At positive temperature one should consider the Gibbs measure $\exp(-\mathcal{H}_N/T)$, as will be discussed later in Section 4.1 below.

In practice the potential V depends on the type of atoms and is not explicitly known. As atoms are not elementary particles, V cannot be deduced from first principles. It is therefore important to obtain mathematical results which are sufficiently generic with regards to V .

Qualitatively, the function V is usually assumed to be non-negative (repulsive) at small distances and negative (attractive) at large distances. Since the interaction between two atoms which are far from each other is small, we assume that $V(r) \rightarrow 0$ as $r \rightarrow +\infty$. A typical and very popular example is the *Lennard-Jones potential*

$$V_{\text{LJ}}(r) = \frac{1}{12} \left(\frac{r_0}{r} \right)^{12} - \frac{1}{6} \left(\frac{r_0}{r} \right)^6, \quad (3)$$

drawn in Figure 1. The behavior at infinity in r^{-6} mimics the Van der Waals interaction, that is, the one for radially symmetric neutral particles. The behavior at $r = 0$ is, on the other hand, completely empirical. The number $r_0 > 0$ is the equilibrium distance for two isolated particles. It may be seen from Figure 1 that for this specific potential in the plane, the solutions x_i to the minimization problem (2) are approximately located on an hexagonal lattice and that they moreover form a big cluster having the shape of an hexagon.

For the rest of the article, we consider a general radial potential V . Some assumptions are however necessary to ensure that our question is well posed.

2.2. Stability. A first assumption, which is related to the behavior of V at the origin, deals with the stability of the system for large N . If the system has a limit as $N \rightarrow +\infty$, it is mandatory that its energy behave linearly with respect to N , that is, the following limit

$$e = \lim_{N \rightarrow +\infty} \frac{E(N)}{N}, \quad (4)$$

should exist. Indeed, if we gather two macroscopic identical systems (for a ‘‘real life’’ object, $N \approx 10^{23}$), the formation energy is equal to $|E(2N) - 2E(N)|$, which may be arbitrarily large if $E(N)$ is not at most linear.

In the present case, since V vanishes at infinity, the energy is sub-additive, that is, it satisfies

$$\forall N, P \in \mathbb{N}, \quad E(N + P) \leq E(N) + E(P). \quad (5)$$

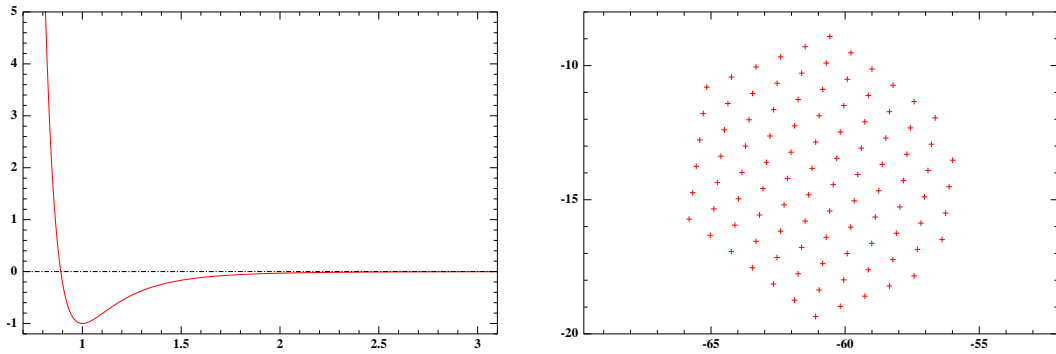


FIGURE 1. Left: the Lennard-Jones potential (3). Right: a minimizer for the variational problem (2), computed numerically in [14], with $N = 100$ and $d = 2$. The particles seem to arrange themselves on an hexagonal lattice, and to form a large cluster having the shape of an hexagon.

This inequality is shown by sending two groups of N and P particles at a large distance from each other. It is classical that, given (5), the existence of the limit (4) is equivalent to the lower bound

$$E(N) \geq -CN \quad (6)$$

or, equivalently,

$$\sum_{1 \leq i < j \leq N} V(|x_i - x_j|) \geq -CN \quad (7)$$

for all N and all $x_1, \dots, x_N \in \mathbb{R}^d$. A potential V satisfying (6) is said to be *stable*. A characterization of the set of stable potentials is an important question which has been widely studied since the 60s [148, 149, 68, 69, 150, 110]. The simplest example of a stable potential is

$$V = V_1 + V_2, \quad \text{with } V_1 \geq 0, \quad \widehat{V}_2 \geq 0 \quad \text{and} \quad \int_{\mathbb{R}^d} \widehat{V}_2 < +\infty,$$

where \widehat{V}_2 denotes the Fourier transform of $x \mapsto V_2(|x|)$, cf. [150, Prop. 3.2.7]. It can be proved that the Lennard-Jones potential (3) is stable in the sense of (6). See for instance [173] for the one-dimensional case. In higher dimension, it is proved in [182, 19] that the distance between two particles of the optimal configuration is bounded from below. Stability then follows easily.

2.3. Formation of a macroscopic object. The assumptions (5)–(6) above imply the existence of a thermodynamic limit (4), but they do not ensure that a macroscopic object is formed in this limit. Their aim is actually to avoid a collapse of the system by preventing particles to be too close to each other. It is still possible that, in the optimal configuration, particles do not stay close to each other. This situation should not be allowed. Indeed, the limit $N \rightarrow \infty$ could be trivial in such a case. For instance, if $V > 0$, then $E(N) = e = 0$ for any $N \in \mathbb{N}$, but the minimization problem (2) has no solution. Indeed, the infimum of $\mathcal{E}_N(x_1, \dots, x_N)$ is reached only when the distances between particles x_i tend to infinity. In principle, it is also possible that the particles want to form groups of K individuals, each of them keeping infinitely far from the others. In such a case, $e = E(K)/K$, and no minimizer exists for $N > K$. The existence of a minimizer is ensured for any N if the inequality (5) is strict whenever $N, P \geq 1$. However, this does not give any information on the way that the particles are distributed in space.

In order to have the formation of a macroscopic object, we want that the minimizing configuration of N particles fill a volume of size N , in the limit $N \rightarrow +\infty$. Moreover, the particles should be evenly spaced in this volume, as it is clear in the example of the Lennard-Jones potential shown in Figure 1.

The mathematical formulation of this property is not unique. One possibility is to apply a dilation of factor $N^{-1/d}$ to the optimal configuration (this is a way to pass to the macroscopic

scale), and to consider the empirical measure

$$M_N = \frac{1}{N} \sum_{i=1}^N \delta_{\frac{x_i}{N^{1/d}}}. \quad (8)$$

We ask if

$$M_N \rightharpoonup M \text{ in the sense of measures, with } M \in L^\infty(\mathbb{R}^d), \text{ supp}(M) \text{ compact, } \int_{\mathbb{R}^d} M(x) dx = 1. \quad (9)$$

This means that the macroscopic object is included in the support of M , and that, at this scale the system is continuous, with the function M as local density. If (9) is satisfied, a macroscopic object has been created. Knowledge about the positions of particles is very crude, because of the dilation of factor $N^{-1/d}$, which does not account for the local behavior of the system. The problem may be formulated differently, keeping track of different scales in the system. However, it becomes more and more difficult as these scales are taken into account.

Finding conditions on the potential which imply the existence of the weak limit (9) is an important problem. However, it has never been, to our knowledge, studied mathematically. For the Lennard-Jones potential V_{LJ} in dimension 2, Figure 1 indicates that the limit M is proportional to the characteristic function of a hexagon. In this example, the shape of the support of M , which is visible at the macroscopic scale (as for instance snow flake structure), is a manifestation of the crystalline structure at the microscopic scale. We will come back to this in Section 3.7 below.

3. THE CRYSTALLIZATION CONJECTURE

3.1. Formulation. We now come to the question which has been intensively studied since the 70s, without being solved. This question is: does the system become periodic in the limit $N \rightarrow \infty$? This may be formulated as follows: Let us denote by

$$\mu_N = \sum_{i=1}^N \delta_{x_i} \quad (10)$$

the empirical measure associated with the solution x_1, \dots, x_N of problem (2). Note that, contrary to (8), we do not use any dilation, and this means that we study the system at the microscopic scale. We ask if, after possibly extracting a subsequence,

$$\mu_N \rightharpoonup \mu \quad (11)$$

locally, where μ is a locally finite measure. We say that crystallization occurs if μ is periodic, that is, if there exists a discrete subgroup

$$G = \left\{ \sum_{j=1}^d n_j v_j, n_j \in \mathbb{Z} \right\} \subset \mathbb{R}^d, \quad (12)$$

generated by d independent vectors $v_1, \dots, v_d \in \mathbb{R}^d$, such that $\mu(\cdot + g) = \mu$ for all $g \in G$. In order to avoid trivial cases, we assume here that G is the maximal group satisfying this property. Put differently, the period is supposed to be minimal. The invariance under the action of G does not imply that the particles are located on the vertices of a periodic lattice. This would correspond to the stronger hypothesis

$$\mu = \sum_{g \in G} \delta_{g+y}, \quad (13)$$

for some fixed vector $y \in \mathbb{R}^d$, defining the position of the lattice in space. For instance, it is possible to have 3 particles in the unit cell of the lattice G , which are repeated periodically, as in Figure 2. In such a case, the configuration of particles is the superposition of 3 shifted crystalline lattices, and the measure has the form

$$\mu = \sum_{g \in G} \delta_{g+y} + \sum_{g \in G} \delta_{g+y+\tau} + \sum_{g \in G} \delta_{g+y+\tau'}.$$

In the special case where the particles are exactly on the nodes of the lattice G , as in (13), we use the word *Bravais lattice* or *mono-atomic lattice*. For instance, in dimension 3, the *simple cubic lattice* (SC), *face-centered cubic lattice* (FCC) and *body-centered cubic lattice* (BCC) are all

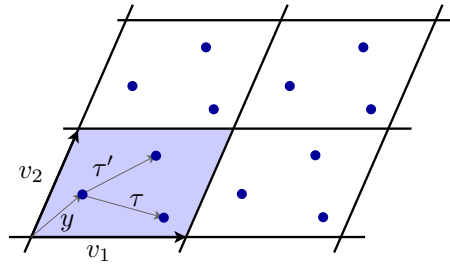


FIGURE 2. Example of a periodic configuration in 2D.

Bravais lattices. On the other hand, the *hexagonal close packed lattice* (HCP) is not. It is the superposition of two shifted Bravais lattices (Figure 3). This configuration is the one used to pile up oranges in markets.

Crystallization may be seen as a symmetry breaking of the system: the invariance of the system under affine isometries is lost in the process. If the positions of the particles form a periodic lattice, then applying a translation, rotation or reflexion to the system does not change its energy. Hence, the set of minimizing lattices has the structure of the compact group $(\mathbb{R}^d/G) \times O_d(\mathbb{R})$. Choosing a special minimizer for the positions x_i at finite N , it is possible to select one of the limiting lattices.

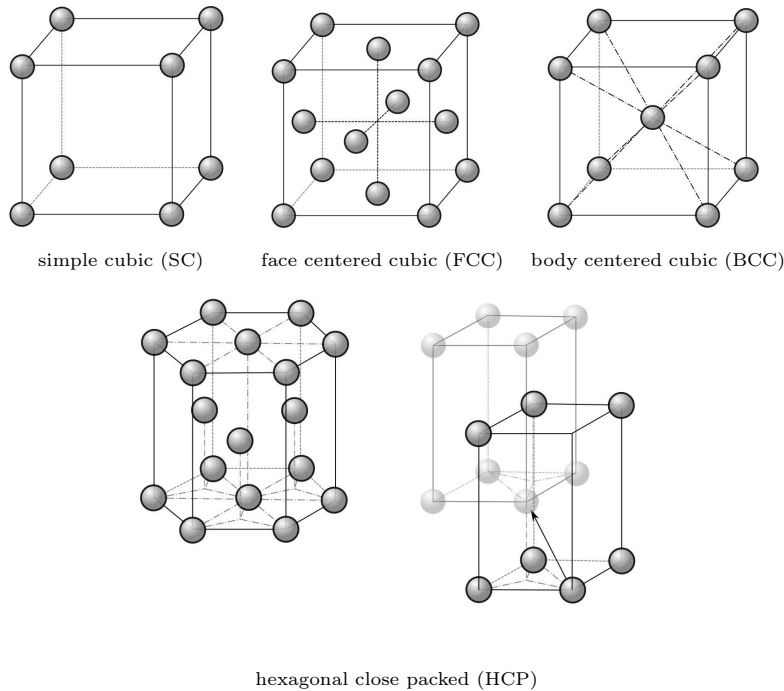


FIGURE 3. Most common configurations in 3D (source: wikipedia).

The microscopic scale convergence (11) does not give any information, in principle, about the behavior at the macroscopic scale, such as the convergence of the dilated measure M_N defined by (9). Conversely, the convergence of M_N does not give any clue about that of μ_N . However, one actually expects that the two phenomenon are related. The understanding of the link between these two scales is still incomplete, as we will discuss in Section 3.7 below.

Should crystallization be proved, the next question is to know which periodic configurations are present in the limit (that is, what is the group G). Another question is to know if μ has the particular form (13) corresponding to a Bravais lattice. If not, one would ask how many particles are present in each periodic cell, and what are their positions. In physical systems, lattices with larger symmetry groups seem to be more common [106]. These lattices are the hexagonal and square lattices in 2D, and the lattices presented in Figure 3 in 3D.

The ubiquity of crystals (at low temperature) indicates that crystallization is a universal phenomenon, which should occur for a wide class of interaction potentials V . As we will see, several mathematical works prove crystallization, but they are based on restrictive assumptions on V . To date, no generic class of potentials has been identified, for which crystallization can be proved.

3.2. Crystallization and sphere packing.

In dimension $d = 1$. In dimension one, the problem of crystallization is rather well understood. The first results are due to Ventevogel and Nijboer [173, 174, 175]: they prove that the limit e is reached by equidistant configurations. This property is proved for a wide class of potentials V (they are assumed to be non-increasing up to a distance $r_0 > 0$, and non-decreasing for $r > r_0$, with additional hypotheses on V''), which includes the Lennard-Jones potential V_{LJ} . The convergence (11) is not proved in these works and is still an open problem. It has been proved in the special case of V_{LJ} by Gardner and Radin [80].

For some explicit examples of potentials V (non-increasing up to a distance $r_0 > 0$, and non-decreasing for $r > r_0$), it has been proved that the optimal configuration does not converge to a Bravais lattice. The limit can be clusters of particles which are globally periodic [173]. With an oscillating potential V , it is even possible to obtain configurations which have no periodicity [94]. In the latter, it is also proved that such aperiodic configurations can be found as minimizers of a potential V which is an arbitrarily small perturbation of a potential for which crystallization occurs. This indicates that crystallization is an unstable property. Thus, the conditions on V ensuring crystallization are probably complex and have not been completely understood yet, even in one dimension. It is commonly assumed that the interaction potential is smooth, stable, non-increasing up to a distance r_0 , and non-decreasing for $r > r_0$. However, no crystallization result has been proved under these assumptions only, even in one dimension.

In dimension $d \geq 2$. In higher dimensions, the problem is far from being understood. Most results are based on geometrical arguments, which allow to reduce the question to a sphere packing problem. This question consists in finding the position of non-overlapping spheres of equal radius giving the largest possible density. In two dimensions, the solution is precisely the hexagonal lattice (see figure 4). Thue has given two proofs of this result (in 1892 and in 1910), which both happened to contain flaws. A proof was then proposed in 1940 by Tóth [144, 49]. In dimension three, the problem is significantly more difficult. Kepler formulated it in 1611, and it is therefore often called *Kepler's conjecture*. A computer-assisted proof was given by Hales in 1999, then published in 2005 in [93]. Only recently (August 2014) has it been fully validated, after eleven years of work by the *Flyspeck* team [71], who managed to give a formal proof based on the softwares *Isabell* and *HOL Light*. An important difference with the two-dimensional case is that, in 3D, the problem has two solutions: the hexagonal close packed lattice and the face centered cubic lattice. The fact that FCC is the unique minimizer among Bravais lattices was proved by Gauss [81].

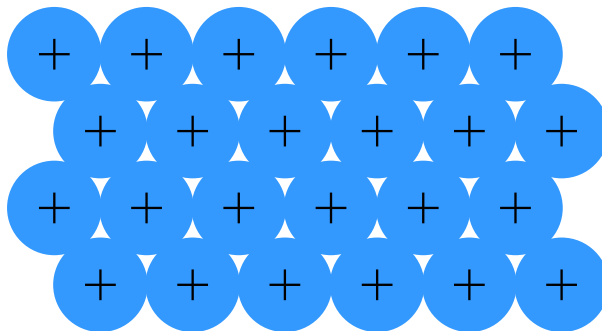


FIGURE 4. Packing of identical disks, maximizing the density. The centers of the disks lie on a hexagonal lattice.

The link between the crystallization problem and the sphere packing problem has been highlighted by Heitmann and Radin in [98]. Indeed, if the interaction potential V is given by

$$V(r) = \begin{cases} +\infty & \text{if } 0 \leq r < 1, \\ -1 & \text{if } r = 1, \\ 0 & \text{if } r > 1, \end{cases} \quad (14)$$

then the particles can be considered as hard spheres of radius $1/2$. These spheres tend to touch due to the condition $V(1) = -1$. The crystallization problem is thus equivalent to the sphere packing, and one obtains that the solution is the hexagonal lattice in 2D and either FCC or HCP in 3D.

Subsequent works aimed at generalizing this result to potentials which are similar to (14), but are closer to physically realistic interactions. For instance, in [138], Radin considers a potential satisfying (14) for $r \in [0, 1]$, which is non-decreasing for $r \geq 1$, and tends to 0 fast enough as $r \rightarrow +\infty$. In a famous article [168], Theil deals with smoother, more realistic potentials (which look like V_{LJ}), in dimension two. However, he uses restrictive hypotheses on V itself. This work has been extended to dimension three recently in [70], in which an additional three-body term is added, which favors particular angles between bonds. A similar strategy has been used in dimension $d = 2$ in [62, 122, 123], where the optimal lattice may be a square lattice. One can therefore consider that the problem is not completely understood in dimension two, and completely open in dimension three.

All these results in dimension two and three rely heavily on the similarity with the sphere packing problem. However, it is not clear if this should be the correct physical explanation. This would exclude, for instance, configurations which are periodic but not mono-atomic. In such a case, particles form small groups which are repeated periodically. The crystallization conjecture for a more general class of potentials is still an open problem.

The sphere packing problem becomes more complex as the dimension increases. Actually, it has been conjectured that crystallization occurs only in small space dimensions [164, 171, 170]. Although the sphere packing problem in high dimension plays an important role in information theory, it is natural to restrict ourselves to the (physically relevant) cases of dimension $d = 1, 2, 3$. This is what we will do in most of the present article.

3.3. A variant: minimization at fixed density. It is possible to consider a potential V which does not allow for the formation of a macroscopic object, as discussed in Section 2.3. Such an example is given, for instance, by a potential $V > 0$ (with $V(r) \rightarrow 0$ as $r \rightarrow +\infty$). In such a case, it is necessary to change the formulation of the problem and the idea is to minimize the energy while keeping the density of particles ρ fixed. This may be done by confining the particles in a large domain Ω and imposing that their number be $N \simeq \rho|\Omega|$, where $|\Omega|$ is the volume of Ω .

To be more precise, we consider the minimization problem for N particles in the domain Ω

$$E_{\Omega}(N) = \inf \left\{ \mathcal{E}_N(x_1, \dots, x_N), \quad x_1, \dots, x_N \in \Omega \right\}, \quad (15)$$

and we study the limit

$$e(\rho) = \lim_{\substack{N \rightarrow \infty \\ |\Omega_N| \rightarrow \infty \\ N/|\Omega_N| \rightarrow \rho}} \frac{E_{\Omega_N}(N)}{N} \quad (16)$$

where $\rho > 0$ is fixed and Ω_N is a sequence of domains which covers the whole space in the limit $N \rightarrow \infty$. Some assumptions are needed on this sequence Ω_N insuring that the limit (16) exists. Further, this limit should not depend on the chosen sequence. For instance, it is often assumed that the measure of the boundary of Ω_N is a lower order term compared to its volume $|\Omega_N|$ [150]. To fix the ideas, one can think of Ω_N as a cube of side length $(N/\rho)^{1/d}$, or a convex symmetric domain of unit volume, dilated by a factor $(N/\rho)^{1/d}$, as for instance a ball of radius $(N/\rho)^{1/d}$.

One then studies the behavior of the particle positions x_1, \dots, x_N solution to the minimization problem (15). The questions are similar to the preceding case. A difference is that the model is no more invariant under affine isometries. Different extraction of the sequence of minimizers may in principle give limiting lattices with different positions. In practice, the position of the limiting lattice is often determined by the choice of a particular sequence Ω_N (see [108] for a discussion of this aspect in dimension $d = 1$).

The fact that one can consider a repulsive potential changes the physical meaning of the problem. In particular, the relation with the sphere packing problem is unclear. In the case of the preceding section, it is natural to consider that the particles are attracted by each others, and behave like hard spheres at short range, therefore trying to maximize the density of the system. Doing so, they tend to maximize the number of neighbours. Here, particles can repel each other fiercely, and tend to maximize their mutual distance, while staying in the domain Ω . Experiments and numerical simulations indicate, however, that here again, crystallization occurs.

In dimension one, Ventevogel and Nijboer have proved crystallization for any density $\rho > 0$ in the case of non-negative non-increasing convex potential [173]. In [174, 175], they prove the same result for the potential $V(x) = \exp(-\alpha x^2)$ and $V(x) = (\beta + x^2)^{-1}$, for $\alpha, \beta > 0$, still in dimension one. This allows to generalize the result to any convex combination of these potential, such as $V(x) = \int_0^{+\infty} e^{-\alpha x^2} d\mu(\alpha)$, for any non-negative measure μ . Such potentials may be non-convex. In addition, they give a necessary condition for crystallization, in any dimension: if crystallization occurs for sufficiently small densities, and V is continuous, then $\widehat{V} \geq 0$. As before, the situation is much less clear in dimension $d \geq 2$.

3.4. Optimal lattices and special functions. If crystallization is *assumed*, it is possible to determine the most favorable periodic configurations by comparing their energy per particle e (defined by (4) and (16)). In some cases, this question may be related to a problem in analytic number theory, involving special functions.

Indeed, if the particles lie on the vertices of a Bravais lattice G (a discrete subgroup of \mathbb{R}^d such as (12)), the limit energy per particle reads:

$$e = \frac{1}{2} \sum_{g \in G \setminus \{0\}} V(g) \quad (17)$$

Finding the optimal configuration amounts to minimize this expression with respect to G . There is no additional constraint on G in the case of a stable potential. In contrast, one needs to fix the volume of the unit cell Q of G to $|Q| = 1/\rho$ when the density is fixed, as for instance in the case of a repulsive potential.

Epstein zeta function. With a Lennard-Jones type potential

$$V(r) = \frac{1}{a} \left(\frac{r_0}{r}\right)^a - \frac{1}{b} \left(\frac{r_0}{r}\right)^b, \quad (18)$$

where $a > b > d$, we get

$$\frac{1}{2} \sum_{g \in G \setminus \{0\}} V_{\text{LJ}}(g) = \frac{\zeta_d(S, a)}{a} - \frac{\zeta_d(S, b)}{b} \quad (19)$$

where S is a symmetric positive definite matrix of size d , which is related to the Gram matrix of the basis $(v_j)_{1 \leq j \leq d}$, and such that $r_0 S^{1/2} \mathbb{Z}^d = G$. Here,

$$\zeta_d(S, s) = \frac{1}{2} \sum_{z \in \mathbb{Z}^d \setminus \{0\}} \frac{1}{(z^T S z)^{s/2}} \quad (20)$$

is the Epstein zeta function [65]. Still assuming that we have crystallization on a Bravais lattice, the minimal energy for V_{LJ} reads

$$e_{\text{LJ}}(a, b) = \min_{S=S^T > 0} \left(\frac{\zeta_d(S, a)}{a} - \frac{\zeta_d(S, b)}{b} \right). \quad (21)$$

Except in dimension $d = 1$, the solution to this problem is still unknown, even for the physically relevant cases $a = 12$ and $b = 6$.

If the density $\rho > 0$ is fixed as discussed in Section 3.3, it is possible to consider a repulsive potential $V(r) = r^{-s}$ with $s > d$. Hence, we need to minimize the value of the zeta function (20), with respect to G (that is, with respect to the matrix S)

$$e_\zeta(\rho, s) = \min_{\substack{S=S^T > 0 \\ \det(S) = \rho^{-2}}} \zeta_d(S, s). \quad (22)$$

Here, $\det(S)$ is the volume of the unit cell of the lattice to the power 2. Applying a dilation of the lattice, one easily proves that

$$e_\zeta(\rho, s) = \rho^{s/d} e_\zeta(1, s)$$

and that it is sufficient to study the problem in which the unit cell has a volume equal to 1. Without loss of generality, we can thus assume that $\det(S) = 1$. There is a link with the sphere packing since, in the limit $s \rightarrow \infty$, the optimal lattice converges to a solution to the d -dimensional sphere packing problem [151]. It should be noted that $\zeta_d(S, s)$ is not bounded. If the smallest eigenvalue of S reaches 0, then $\zeta_d(S, s)$ tends to $+\infty$.

The function $s \mapsto \zeta_d(S, s)$ has an analytic continuation to the set $\mathbb{C} \setminus \{d\}$. This extension has a simple pole at $s = d$, with a residue equal to $\pi^{d/2} \Gamma(d/2)^{-1}$ (if $\det(S) = 1$), and satisfies the functional equation

$$\zeta_d(S, s) = \pi^{s-d/2} \frac{\Gamma(\frac{d-s}{2})}{\Gamma(\frac{s}{2})} \zeta_d(S^{-1}, d-s) \quad (23)$$

where S^{-1} is the matrix associated with the lattice $G^* = \{k \in \mathbb{R}^d : k \cdot g \in \mathbb{Z}, \forall g \in G\}$, called the *dual lattice of G* [29, 28]. Thus, it is also possible to study the minimization problem (22) even if $0 < s < d$. As we will see below, this problem is of great importance from a physical point of view, particularly if $d = 3$ and $s = 1$. Formula (23) implies that if S is a solution to the minimization problem $e_\zeta(1, s)$, then S^{-1} is a solution to $e_\zeta(1, d-s)$.

Going back to the case of the Lennard-Jones potential (21), we see that, after dilating the problem with fixed density $\rho > 0$, it amounts to minimize the function

$$\rho^{a/d} \left(\frac{\zeta_d(S, a)}{a} - \rho^{\frac{b-a}{d}} \frac{\zeta_d(S, b)}{b} \right)$$

with respect to S , with $\det(S) = 1$. Since $b > a$ is assumed, for large ρ the problem reduces to the minimization of $\zeta_d(S, a)$. For small values of ρ , the situation is not that clear, since ζ_d is not bounded from above. For the minimization problem (21) with no density constraint, one finally needs to consider ρ which minimizes the energy. In this case, the optimal lattice is unknown.

One can derive representation of ζ_d as a series with exponentially decaying coefficients. The most widely used method for this is that of Ewald [66, 24, 87] which uses the integral representation

$$\frac{1}{r^s} = \frac{1}{2\Gamma(s/2)} \int_0^\infty e^{-\tau r^2} \tau^{s/2-1} d\tau. \quad (24)$$

For $s > d$, we have, if $\det(S) = 1$,

$$\zeta_d(S, s) = \frac{\pi^{s/2}}{\Gamma(s/2)} \left\{ \frac{1}{s-d} - \frac{1}{s} + \frac{1}{2} \int_1^\infty \left((\theta_d(S, \tau) - 1) \tau^{s/2-1} + (\theta_d(S^{-1}, \tau) - 1) \tau^{\frac{d-s}{2}-1} \right) d\tau \right\} \quad (25)$$

where

$$\theta_d(S, \alpha) = \sum_{z \in \mathbb{Z}^d} e^{-\pi \alpha z^T S z}. \quad (26)$$

is the *Jacobi theta* function. Here, we have used Poisson's summation formula

$$\theta_d(S, \alpha) = \frac{1}{\alpha^{d/2}} \theta_d \left(S^{-1}, \frac{1}{\alpha} \right). \quad (27)$$

Formula (25) is also meaningful for $0 < s < d$ and can be used to prove that ζ_d has an analytic extension to $\mathbb{C} \setminus \{d\}$ (Γ has a pole at the origin which compensates the divergent term $1/s$), as we already mentioned.

Formula (25) is widely used by physicists. It allows to compute numerically the values of $\zeta_d(S, s)$ very accurately, allowing to formulate conjectures on what should be proved. The mathematical literature on the subject is rather poor, so we are now going to describe what is expected.

Results for ζ and θ in dimension 2. In dimension $d = 2$, it has been proved by Rankin [142], Cassels [40], Ennola [63] and Diananda [53], that the hexagonal lattice is the unique minimizer of zeta function, for any $s > 0$, when the density is fixed. In other words, we have

$$\zeta_2(S, s) - \zeta_2(S_{\text{hex}}, s) \geq 0 \quad (28)$$

for all $s > 0$ and all S such that $\det(S) = 1$, where

$$S_{\text{hex}} = \frac{2}{\sqrt{3}} \begin{pmatrix} 1 & 1/2 \\ 1/2 & 1 \end{pmatrix}$$

corresponds to the hexagonal lattice. In addition, the inequality (28) is strict if $S \neq S_{\text{hex}}$, up to the invariances of the problem (rotation and change of basis of the lattice). This result is illustrated in Figure 5. Another proof is given in [131]. Inequality (28) is still valid for $s = 2$ where both functions have a simple pole with equal residue. When $s \rightarrow 0$, we have a divergence which needs to be dealt with, but the result is still true [155].

A famous result due to Montgomery [128] deals with the case of a Gaussian repulsive interaction in dimension $d = 2$. In this case, the problem reduces to the study of the Jacobi theta function (26). As for the zeta function, Montgomery proves that $\theta_2(S, \alpha) \geq \theta_2(S_{\text{hex}}, \alpha)$ for all $\alpha > 0$ and all S such that $\det(S) = 1$ (cf. Figure 6). If the potential V is a positive linear combination of Gaussians, Montgomery's result implies that the optimal lattice is the hexagonal one, for a fixed unit cell volume. For instance, using the integral formula (25), one recovers the previously mentioned result on zeta functions.

Subtracting two Epstein zeta functions gives a function that can be expressed as an integral of the function $\theta_2(S, \alpha)$ multiplied by a weight. This weight is non-negative when ρ is large enough. Using this argument, Bétermin and Zhang [16] have proved that, at high density, the optimum is reached by the hexagonal lattice in 2D, for the Lennard-Jones potential V_{LJ} . Imposing that ρ is large means that particles are close to each other. Therefore, their interaction is dominated by the repulsive part r^{-12} of V_{LJ} . The energy is close to $\zeta_2(S, 12)$, which, as a function of S , reaches its minimum for the hexagonal lattice only. On the contrary, they prove that, when $\rho \rightarrow 0$, the hexagonal lattice cannot be the global minimizer. For instance, if

$$\rho^3 < \frac{\zeta_2(I_2, 6) - \zeta_2(S_{\text{hex}}, 6)}{\zeta_2(I_2, 12) - \zeta_2(S_{\text{hex}}, 12)},$$

the square lattice ($S_{\text{car}} = I_2$) has an energy which is smaller than that of the hexagonal lattice. If no symmetry breaking occurs, then the square lattice becomes the minimizer. This work does not give any information on the global minimizer of the Lennard-Jones potential in 2D: in such a case, one needs to minimize over ρ , too. For a more recent work in the same spirit, see [15].

Results and conjectures for ζ and θ in dimension $d \geq 3$. In dimension $d \geq 3$, some authors have studied the critical points and the (local or global) minima of the Jacobi theta function and the Epstein zeta function. In a famous article [159], Sarnak and Strömbergsson were able to completely solve the problem in dimensions 4, 8 and 24 (see also [50, 48, 51]). In dimension 3, Ennola has proved that the face centered cubic (FCC) lattice is a non-degenerate local minimum of $\zeta_3(S, s)$ for all $s > 0$ [64]. Formula (23) implies that its dual, the BCC lattice, is also a non-degenerate local minimum for $0 < s < 3$. In addition, based on the sphere packing problem obtained in the limit $s \rightarrow \infty$, it has been shown in [151] that FCC is the unique global minimizer for s large enough. As opposed to what Ennola conjectured in [64], FCC cannot be the unique minimizer for all $s > 0$. Indeed, formula (23) would imply that its dual, BCC, is a minimizer for some values of s . Hence, a more likely conjecture would be that FCC is the unique minimizer for $s > 3/2$, whereas BCC is for $0 < s < 3/2$ [159, section 5].¹ If it is assumed that the minimizer has a high-symmetry group, and if we only compare the energies of SC, FCC and BCC, this conjecture is corroborated by numerical computations presented in Figure 7. It is a very important conjecture: its proof would be an important advance both in analytic number theory and in solid-state physics. One of the difficulties in the proof is that the values of the zeta function for BCC and FCC are very close to each other. This implies that a quantitative argument needs to be very precise.

Similar questions may be asked about theta function (26), but it seems that the corresponding literature is far less important. In 3D, the conjecture is that FCC is the unique minimizer for any $\alpha > 1$, whereas BCC is for $\alpha < 1$ [159, section 5]. Here again, this conjecture is confirmed by numerical simulations presented in Figure 8. Note that, contrary to dimension 2, the conjecture for the theta function does not seem to imply it for the zeta function: formula (24) always involves both the lattice and its dual for different values of α .

¹Note that BCC cannot be a non-degenerate local minimum for all $s > 0$ [67, 91], hence it has to be a degenerate critical point of ζ_d for some $s \geq 3$.

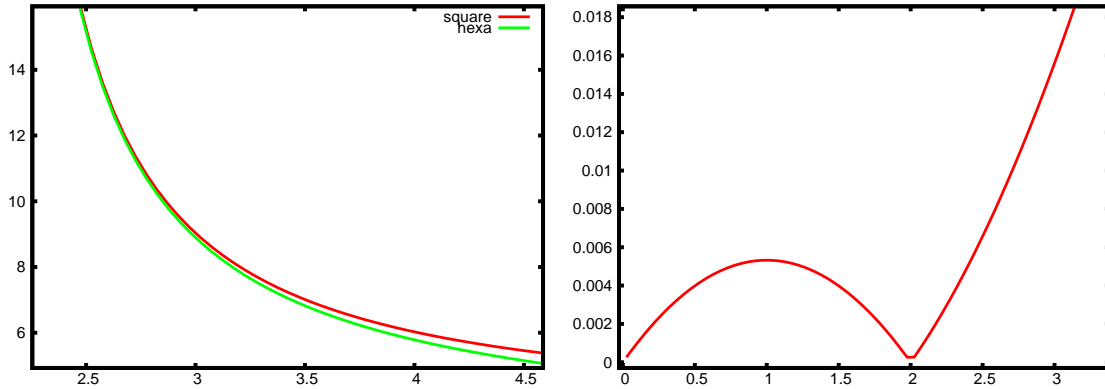


FIGURE 5. Left: $\zeta_2(S, s)$ as a function of s for the square lattice ($S = I_2$) and the hexagonal one ($S = S_{\text{hex}}$). Right: the relative difference $(\zeta_2(I_2, s) - \zeta_2(S_{\text{hex}}, s))/|\zeta_2(S_{\text{hex}}, s)|$. It shows that the hexagonal lattice energy is lower than that of the square lattice for all $s > 0$, as it is proved in [142, 40, 63, 53].

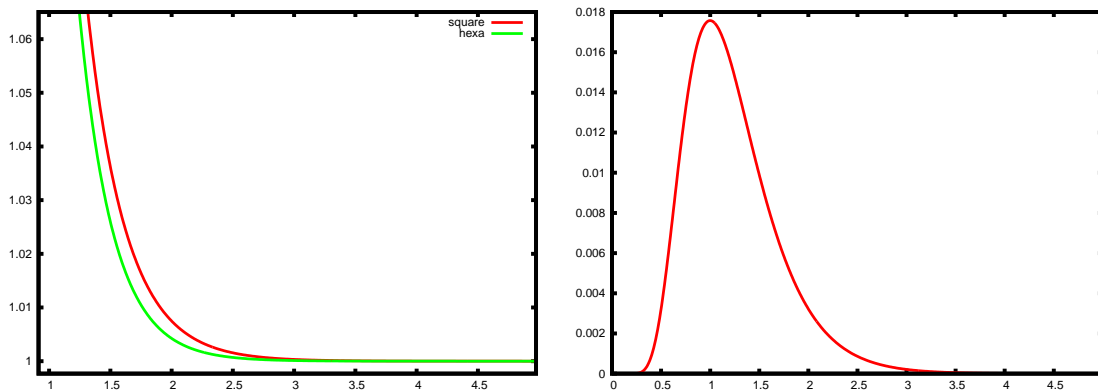


FIGURE 6. Left: $\theta_2(\alpha)$ as a function of α for the square lattice ($S = I_2$) and the hexagonal one ($S = S_{\text{hex}}$). Right: the relative difference $(\theta_2(I_2, \alpha) - \theta_2(S_{\text{hex}}, \alpha))/\theta_2(S_{\text{hex}}, \alpha)$. It shows that the hexagonal lattice energy is lower than that of the square lattice for all $s > 0$, as it is proved in [128].

Most works consider only mono-atomic lattices. This excludes the HCP (Hexagonal Close Packed) lattice in dimension 3, since it is not a Bravais lattice. We refer to [121] for an explicit link between zeta functions and quantum field theory, to [166] for the link with optimal quadrature point repartition, and to [134, 158, 159] for the link with the optimization of the determinant of the Laplace operator: $\det(-\Delta) = e^{-\zeta'_d(S, 0)}$.

As a conclusion, determining the optimal periodic lattice can, for some simple potentials, be related to the study of special functions. the conjecture is that the minimizer can be either the FCC lattice, or the BCC one. This is still an open problem (in most cases), even though research is very active on this subject.

3.5. Coulomb potential and Wigner crystallization. In the case of a strongly repulsive potential V , the problem of minimizing the energy at fixed density (as described in Section 3.3) is in general not physically relevant. Indeed, it is not clear how the particles can be maintained in the domain Ω , despite their strong repulsion. Another approach was proposed by Wigner [178] in 1934 in the particular case of Coulomb repulsion. Wigner's objective was the description of electrons in a metal. These particles do not move in vacuum, but in a charged background compensating the charge of the electrons. If the electrons repel each other, they are attracted by this background and an equilibrium is possible, even for a repulsive potential.

To simplify the setting, it is often assumed that the background is homogeneous, of density $\rho > 0$. This is the so-called *Jellium* model, in which the background is a kind of “jelly” slowing

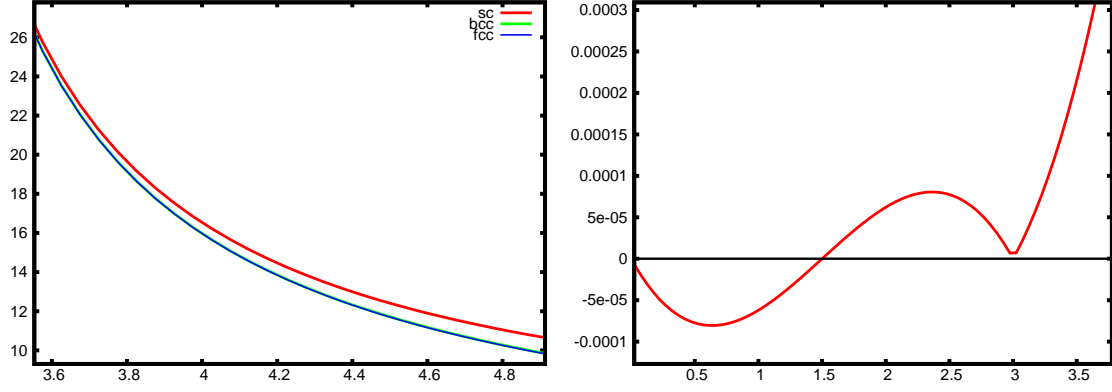


FIGURE 7. Left: $\zeta_3(S, s)$ as a function of s for different lattices ; FCC and BCC have energies which are very close to each other. Right: the relative difference $(\zeta_3(\text{BCC}, s) - \zeta_3(\text{FCC}, s)) / |\zeta_3(\text{FCC}, s)|$. It indicates that BCC should be the minimizer for $0 < s < 3/2$, while FCC should be for $s > 3/2$. Proving this is still an open problem. The relative difference is of order 10^{-4} .

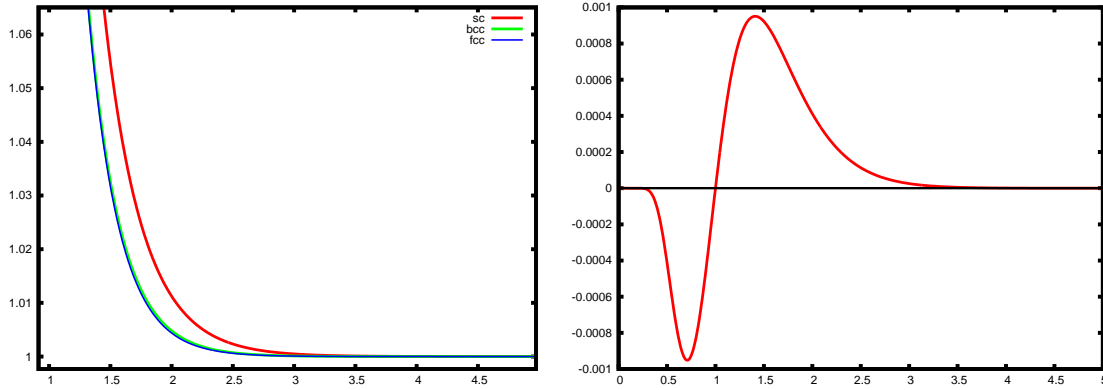


FIGURE 8. Left: $\theta_3(\alpha)$ as a function of α for several lattices ; FCC and BCC have energies which are very close to each other. Right: the relative difference $(\theta_3(\text{BCC}, \alpha) - \theta_3(\text{FCC}, \alpha)) / \theta_3(\text{FCC}, \alpha)$. It indicates that FCC is the minimizer for $\alpha > 1$, while BCC is for $\alpha < 1$. Proving this is an open problem, which does not seem to imply the above result on the function ζ_3 .

down the movements of the particles. The minimization problem then reads:

$$E_{\Omega, \rho}(N) = \inf_{x_1, \dots, x_N \in \Omega} \left\{ \sum_{1 \leq i < j \leq N} V(|x_i - x_j|) - \rho \sum_{i=1}^N \int_{\Omega} V(x_i - y) dy + \frac{\rho^2}{2} \int_{\Omega} \int_{\Omega} V(|x - y|) dx dy \right\} \quad (29)$$

with the same limit as before

$$e_{\text{Jell}}(\rho) = \lim_{\substack{N \rightarrow \infty \\ |\Omega_N| \rightarrow \infty \\ N/|\Omega_N| \rightarrow \rho}} \frac{E_{\Omega_N, \rho}(N)}{N}. \quad (30)$$

The second term of the energy in (29) accounts for the interaction of our N particles with the homogeneous background. This is a new term compared to the preceding cases. The last term is the energy of the background, which is constant with respect to the positions of the particles. We keep it in order to have a finite limit (30) (in the case we deal with here, $\int_{\Omega} \int_{\Omega} V(|x - y|) dx dy$ grows faster than $|\Omega|$ since V is not integrable). In the limit (30) one imposes that $N/|\Omega_N| \rightarrow \rho$, which means that the particle density is equal to that of the background. This allows to reach an electrostatic equilibrium between particle repulsion and the attraction of the background. One could in principle minimize over the domain Ω while fixing $|\Omega| = N\rho$, and then use this domain

Ω_N , but it is often assumed that Ω_N has a shape which is fixed (a cube or a ball for instance), and is then dilated. The limit (30) should not depend on the chosen sequence Ω_N .

In principle, one could use any potential V , but originally Wigner was interested in the electrostatic interaction between electrons, that is, Coulomb potential in dimension $d = 3$:

$$V_{\text{Coul},3\text{D}}(x) = \frac{1}{|x|}.$$

More generally, the Coulomb potential in dimension d is the Green function of the Laplace operator, that is, the solution to

$$-\Delta V_{\text{Coul}} = |S^{d-1}| \delta_0,$$

in the sense of distribution, where $|S^{d-1}|$ is the volume of the sphere in dimension d , $S^{d-1} = \{x \in \mathbb{R}^d : |x| = 1\}$. In lower dimension, we thus have $V_{\text{Coul},1\text{D}}(x) = -|x|$ and $V_{\text{Coul},2\text{D}}(x) = -\log|x|$.

In [178], Wigner has conjectured crystallization for this model, at least if ρ is small enough. He also suggested that in 3D, the electrons form a body centered cubic lattice (BCC). In 2D, the particles are expected to form a hexagonal lattice. Numerical simulations and formal computations corroborate Wigner's conjecture. However, a rigorous proof is still missing in dimension $d \geq 2$.

Dimension $d = 1$ is simpler and has been solved by Kunz in 1974 for small densities [108]. This result has been generalized to any density by Aizenman and Martin [4]. At temperature $T = 0$, the particles form a lattice of step $1/\rho$, as in the preceding sections. If $T > 0$, it has also been proved in [4] that the particle density is periodic of period $1/\rho$. A different proof, which applies to the quantum case, has been proposed by Brascamp and Lieb in [31]. It is an application of their study of the optimality of Gaussians in some functional inequalities.

As in Section 3.4, if crystallization is assumed (on a Bravais lattice G), it is possible to compute the corresponding energy per unit volume. In the present case, we have

$$e_{\text{Jell},G}(\rho) = \frac{1}{2} \sum_{g \in G \setminus \{0\}} W_{\text{Coul}}(g) - \int_Q V_{\text{Coul}}(x) dx + \frac{\rho}{2} \int_Q \int_Q V_{\text{Coul}}(x-y) dx dy \quad (31)$$

where W_{Coul} is the twice-screened Coulomb potential

$$W_{\text{Coul}}(x) = V_{\text{Coul}}(x) - 2 \frac{1}{|Q|} \int_Q V_{\text{Coul}}(x-y) dy + \frac{1}{|Q|^2} \int_Q \int_Q V_{\text{Coul}}(x+y-z) dy dz$$

with Q the unit cell of the lattice G , satisfying $|Q| = 1/\rho$. The series (31) is oscillating and its convergence depends on the symmetry properties of the unit cell Q , which determine the decay of W_{Coul} at infinity. In dimension $d = 3$, it is sufficient to choose for Q a set which is symmetric with respect to the origin 0, which is always possible. Doing so, W_{Coul} behaves like $|x|^{-4}$ at infinity. If Q has sufficient symmetry properties, it is possible to express the energy with the simple screened Coulomb potential

$$\tilde{W}_{\text{Coul}}(x) = V_{\text{Coul}}(x) - \frac{1}{|Q|} \int_Q V_{\text{Coul}}(x-y) dy.$$

We refer to [113, App. B] for the details. It is always useful to use for Q the Wigner-Seitz cell, which has the same symmetries as the lattice G [12].

When the series above converge, one can prove that the energy (31) is *equal to the analytic extension of the first term in (29)*, that is,

$$\boxed{e_{\text{Jell},G}(\rho) = \zeta_d(S, d-2)}, \quad (32)$$

for $d > 2$. The proof is based on the same arguments as [113, App. B], and on results from [27, 26, 28]. In a way, the second and third terms of the energy in (29) are only useful to give a meaning to the problem. They vanish in the limit $N \rightarrow +\infty$. The point $s = d-2$ is always smaller than the pole $s = d$, hence the importance of studying the zeta function at this point. For $d = 3$, the numerical simulations presented in this article indicate that the body centered cubic lattice (BCC) is the unique global minimizer, as conjectured by Wigner. Proving this fact is still an open problem. In dimension $d = 2$, the energy has a logarithmic singularity which needs to be removed, but the problem is similar. In [155], Sandier and Serfaty used Montgomery's result to prove that the optimal lattice in 2D is the hexagonal lattice, in the limit $s \rightarrow 0$.

Physicists usually rely on the integral representation (24) to compute the value of the zeta function and compare different lattices. As an example, the energies are approximately equal to

$$-\rho^{1/3} \begin{cases} 1.41865\dots & \text{for the simple cubic lattice (SC),} \\ 1.44415\dots & \text{for the face centered cubic lattice (FCC),} \\ 1.44423\dots & \text{for the body centered cubic lattice (BCC),} \end{cases}$$

in dimension $d = 3$ [29, 87]. Using an argument due to Onsager [133], Lieb and Narnhofer managed to prove in [118] that the true energy defined by (30) satisfies $e_{\text{Jell}}(\rho) \geq -\rho^{1/3}1.4508\dots$ for any $\rho > 0$. This value is very close to the expected one. However, the proof of Wigner crystallization is still an open problem, in dimension $d \geq 2$.

Let us point out that Wigner's model has been recently studied and reformulated in [157, 147, 136]. In these articles, the energy $e_{\text{Jell}}(\rho)$ is called *renormalized energy* and is defined directly on sets of points (which need not be periodic), without using the thermodynamic limit $N \rightarrow \infty$.

3.6. Crystallization problem in other situations. In this section, we present a few questions that can be formulated as crystallization problems, as stated above, or as Wigner's problem. This shows that the problem is universal.

3.6.1. Confined systems in the mean-field limit. The crystallization problem appears in highly dense systems. Here, a change of scale is needed so that we recover a problem set in the whole space. The prototypical situation is to minimize the energy

$$E_{V_{\text{ext}}}(N) = \min_{x_i} \left\{ \frac{1}{N} \sum_{1 \leq i < j \leq N} V(x_i - x_j) + \sum_{i=1}^N V_{\text{ext}}(x_i) \right\}, \quad (33)$$

where V_{ext} is a confining potential, which tends to $+\infty$ at infinity. The coefficient $1/N$ multiplying the interaction allows for both terms to be of the same order of magnitude in the limit $N \rightarrow +\infty$. This is called the *mean field* regime. An example of interaction V is given by $V(x) = |x|^{-s}$ with $0 < s < d$, or $V(x) = -\log|x|$. Most commonly used confining potentials are the harmonic potential $V_{\text{ext}}(x) = |x|^2$, and the potential

$$V_{\text{ext}}(x) = \begin{cases} 0 & \text{if } x \in \mathcal{M}, \\ +\infty & \text{otherwise,} \end{cases}$$

which amounts to impose that all the particles stay in the set $\mathcal{M} \subset \mathbb{R}^d$. The set \mathcal{M} can be a bounded domain like a ball, or a zero-measure set such as a sub-manifold of \mathbb{R}^d , of dimension strictly smaller than d .

If $d = 3$ and $\mathcal{M} = S^2$ is the unit sphere, and if $V(x) = |x|^{-1}$, the problem is referred to as *Thomson problem* [169]. Finding the optimal positions of the particles on the sphere, even for a fixed value of N , is a famous problem which has been solved only for some values of N . Many numerical studies of the problem have been proposed, giving some insight on what the optimal configuration should look like. This problem is one of the eighteen open problems mentioned by Smale in 1998 in [165]. It naturally occurs in many different situations: it is related to the construction of a set of points which discretizes the sphere as uniformly as possible (the so-called Fekete points [152]); in biology, this problem can explain the form of some viruses, and the repartition of pores on pollen grains; it is also studied in link with "colloidosomes" [54] (Figure 9). If $V(x) = |x|^{-s}$, with $d > s$, and if \mathcal{M} is a sub-manifold without boundary, of dimension $d - 1$, the problem is usually called *Riesz problem*. We refer to [96] for a general presentation of the problem and numerical simulations.

For the model (33), a second-order expansion is needed to find the crystallization problem. Indeed, the leading order is, under appropriate assumptions, given by the mean-field theory

$$\lim_{N \rightarrow \infty} \frac{E_{V_{\text{ext}}}(N)}{N} = \inf_{\substack{\sigma \text{ probability} \\ \text{measure on } \mathbb{R}^d}} \left\{ \frac{1}{2} \int \int V(x - y) d\sigma(x) d\sigma(y) + \int V_{\text{ext}}(x) d\sigma(x) \right\}. \quad (34)$$

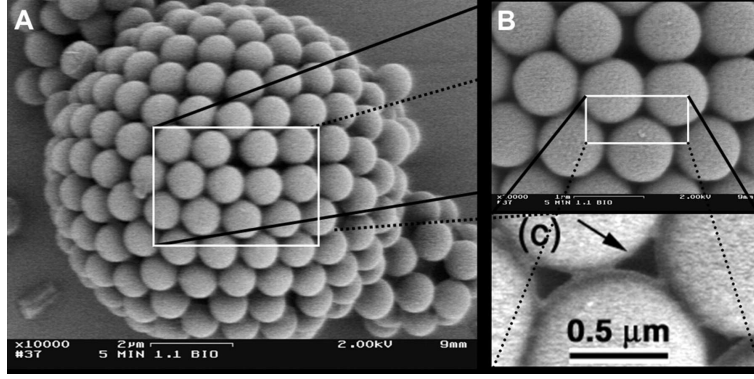


FIGURE 9. A colloidosome is a spherical shape made of colloids (polystyrene molecules here), which is described by Thomson model. This model consists in minimizing the interaction $|x|^{-s}$ for particles on the sphere $S^2 \subset \mathbb{R}^3$. Scanning microscope picture, from [54]. © Picture reproduced with the authorization of the AAAS.

The measure σ , solution to this variational problem, is in general absolutely continuous with respect to the Lebesgue measure, and gives the average repartition of the points in space. More specifically,

$$\frac{1}{N} \sum_{i=1}^N \delta_{x_i} \rightarrow \sigma \quad (35)$$

in the sense of measures. Since in \mathbb{R}^d the points x_i will have a typical distance of order $N^{-1/d}$, the measure σ plays the same role as the macroscopic measure M discussed in (8)–(9). For instance, in the case of Thomson problem for which V_{ext} confines the particles to the unit sphere S^2 and $V(x) = |x|^{-1}$, the solution is unique and equal to the uniform measure $\sigma = (4\pi)^{-1}$ on S^2 . This means that the particles tend to be uniformly distributed on the sphere. For a general set \mathcal{M} or general confining potential V_{ext} , proofs of (34) and (35) are given in [47, 109, 127, 37, 38, 104, 105, 146].

A change of scale is needed to be able to study accurately how particles are organized at the microscopic scale. In order to do so, it is better if the potential V behaves appropriately under dilations. In general, one assumes that $V(x) = |x|^{-s}$ (or $V(x) = -\log|x|$, which formally corresponds to the case $s = 0$). When V_{ext} is smooth, after a dilation of $N^{-1/d}$ around a given point $\bar{x} \in \mathbb{R}^d$, the problem may be reformulated as Wigner's problem in dimension d , with the local density $\rho = \sigma(\bar{x})$. The total limit energy is the superposition of these local problems, and one finds

$$E_{V_{\text{ext}}}(N) = aN + N^{\frac{s}{d}} e_{\text{Jell}}(1) \int_{\mathbb{R}^d} \sigma(x)^{1+\frac{s}{d}} dx + o(N^{\frac{s}{d}})$$

where a is the constant given by (34), and where $e_{\text{Jell}}(1)$ is the Jellium energy (30) for $\rho = 1$ with interaction $V(x) = |x|^{-s}$ (this expansion is modified in the case $V(x) = -\log|x|$). This result has been recently proved by [157, 156, 145] in the case $V(x) = -\log|x|$ in dimensions $d = 1, 2$, in [147] for the Coulomb potential $s = d - 2$, and in [136] for $d - 2 < s < d$.

In the case of a sub-manifold $\mathcal{M} \subset \mathbb{R}^d$, the scaling is modified, and one applies a dilation of $N^{-1/d'}$ where d' is the dimension of \mathcal{M} . It is expected that the same kind of results hold [176, 177, 88, 141, 32, 33], although it has not been proved yet, except in the case of the sphere in dimension $d = 2$ with $V(x) = -\log|x|$ [36].

The asymptotics $O(N)$ in (34) is only valid if V is locally integrable, so that the right-hand side is finite. Several authors have studied the case of a potential which is not locally integrable, typically $V(x) = |x|^{-s}$ for $s \geq d$. In the case of a submanifold \mathcal{M} of dimension d' , the corresponding energy behaves like $N^{s/d'}$ (or $N \log N$ for $s = d'$). If $s > d'$, it was proved in [107, 92, 97, 124, 25] that the corresponding term reads

$$\lim_{N \rightarrow \infty} \frac{E_{V_{\text{ext}}}(N)}{N^{s/d'}} = |\mathcal{M}|^{-s/d'} e(1), \quad (36)$$

where $e(1)$ is the minimal energy (16) corresponding to the crystallization problem on the whole space with $V(x) = |x|^{-s}$:

$$e(1) = \lim_{\substack{N \rightarrow \infty \\ |\Omega_N| \rightarrow \infty \\ N/|\Omega_N| \rightarrow 1}} \left(\frac{1}{N} \inf \left\{ \sum_{1 \leq i < j \leq N} |x_i - x_j|^{-s}, x_i \in \Omega_N \right\} \right).$$

As we pointed out in Section 3.4, the conjecture is that the particles are located on a hexagonal lattice in dimension $d' = 2$ and FCC when $d' = 3$. In such a case, the right-hand side is equal to $\zeta_{d'}(S, s)$ with S corresponding to the optimal lattice.

Except in dimension 1 [156, 111] for which the crystallization problem is better understood, it seems that none of these works provide any new information on the crystal problem itself. Nevertheless, they give an insight on how the crystallization problem naturally appears in many different situations.

3.6.2. Vortices and crystallization in dimension 2. In dimension $d = 2$, the crystallization problem surprisingly appears when studying fast rotating Bose-Einstein condensates or superconductors in large magnetic field. Vortices are created, and their number grows with the rotation speed (or the magnetic field intensity). When this number becomes large, they seem to form a hexagonal lattice, called *Abrikosov lattice* in this context [2].

In fast rotating Bose-Einstein condensates, vortices may be modeled as particles interacting via a potential. The corresponding energy may be computed using Jacobi theta function (26) [3]. In this context, Montgomery's result explains why the vortices should form a hexagonal lattice (see Figure 10).

Vortex patterns for the Ginzburg-Landau equation of superconductivity have been widely studied in the mathematics literature (see [17, 18], the first articles on the subject, using simplified models). Under some constraints on the magnetic field, there is a finite number of vortices which behave like classical particles interacting via the (two-dimensional) Coulomb potential and submitted to a harmonic confining potential [153, 100, 162, 161, 154]. For extremely intense magnetic fields, the number of vortices tends to infinity, and the limit problem becomes that of Wigner's crystallization (see Section 3.5), as shown in [155]. This explains, although it has not been proved rigorously yet, why the hexagonal lattice appears in superconductors. We refer to [163] for a more detailed presentation of this problem.

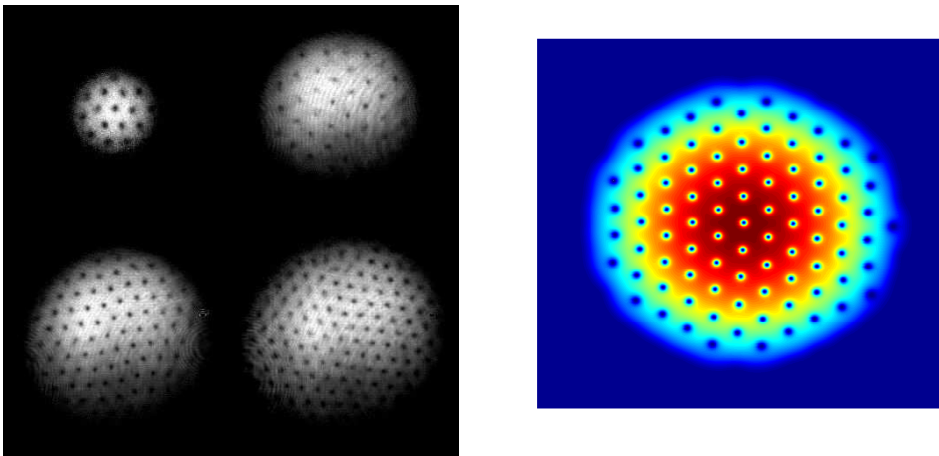


FIGURE 10. *Left:* Experimental pictures of fast rotating Bose-Einstein condensates: the number of vortices increases with the rotation velocity. The experiments have been conducted by Ketterle's team [1] at MIT in 2001. © Picture reproduced with the authorization of the AAAS. *Right:* Numerical simulation of the Gross-Pitaevskii equation with the software GPESLab [10, 11], reproducing the vortex lattice in the corresponding regime.

3.6.3. *Ohta-Kawasaki model.* The Ohta-Kawasaki model describes phase separation in copolymer systems [132]. In its simplest version, it consists in minimizing the energy functional

$$\varepsilon |\partial E| + \frac{1}{2} \int_{\Omega} \int_{\Omega} (u(x) - \bar{u})V(x-y)(u(y) - \bar{u}) dx dy$$

where Ω is a bounded domain of \mathbb{R}^d and where u is allowed to take only the two values ± 1 , each one corresponding to a phase of the system. The potential V is often assumed to be the Coulomb or Yukawa interaction, with periodic boundary conditions on Ω if it happens to be a cube. One then investigates the optimal configurations, as the parameters ε and \bar{u} vary. If $\bar{u} = -1$, then the energy simplifies into

$$\varepsilon |\partial E| + 2 \int_E \int_E V(x-y) dx dy. \quad (37)$$

A regularized version of the model consists in minimizing the energy functional

$$\int_{\Omega} \left(\varepsilon^2 |\nabla u(x)|^2 + F(u(x)) \right) dx + \int_{\Omega} \int_{\Omega} (u(x) - \bar{u})V(x-y)(u(y) - \bar{u}) dx dy,$$

where F is a non-negative function having as unique minimum points $u = \pm 1$. In the limit $\varepsilon \rightarrow 0$, this problem becomes equivalent to (37).

In dimension one, it has been proved that the minimizer is periodic [129, 8, 143, 45, 183, 84] if $\bar{u} = 0$, for all $\varepsilon > 0$. Very few results exist in higher dimension [7, 46]. In the limit where one phase is strongly favored ($\bar{u} \sim 1$) and $\varepsilon \rightarrow 0$, it has been proved that, here again, the opposite phase -1 is a solution to Wigner crystallization problem [89, 90].

A proof of crystallization on the hexagonal lattice (in 2D) has been recently given in [30] for a different copolymer model. In this theory, the second term in (37) is replaced by the Wasserstein distance \mathcal{W} to the Lebesgue measure. Hence, the energy is defined for point measures μ having their support in $\Omega \subset \mathbb{R}^2$. It reads

$$\mathcal{E}(\mu) = \varepsilon \sum_{z \in \text{supp}(\mu)} \sqrt{\mu(\{z\})} + \mathcal{W}(\mathbb{1}_{\Omega}, \mu),$$

and crystallization is proved for any $\varepsilon > 0$ if Ω has appropriate symmetries, and if ε is sufficiently small (or equivalently if $\varepsilon > 0$ is fixed and $|\Omega| \rightarrow \infty$). In the limit $\varepsilon \rightarrow 0$ it had been proved previously that the hexagonal lattice minimizes the Wasserstein distance to the Lebesgue measure [130].

3.7. The macroscopic object and its microscopic structure. We mentioned above the question of proving the existence of a macroscopic measure M , obtained as the weak limit (9). This is related to the formation of a macroscopic object. Another question is to know what kind of object is formed, that is, to compute the measure M .

This problem seems different from the local behavior of the particles. However, the hexagon in Figure 1 indicates that a link exists with the microscopic scale. Indeed, if exact crystallization is assumed, that is, if the particles are restricted to be on the vertices of a periodic lattice for all N , then it is possible to write a limit minimization problem for the surface energy, which coincides with the second-order term in the development of $E(N)$. This term is of order $N^{(d-1)/d}$. It has been proposed by Wulff [181], and proved rigorously for a hard sphere model² in dimension two by Au Yeung, Friesecke et Schmidt in [13, 160]. This work is based on results by Radin et al [138, 98]. We refer for instance to [22, 21, 44] for similar results on the Ising model, based on probabilistic techniques.

These works *assume* that the particles form a subset of a given periodic lattice for all N , which is true only for very specific interaction potentials V . It would be interesting to generalize these results to more general cases. However, this problem is *a priori* a very difficult one, since a good knowledge of the leading order term of $E(N)$ is needed to understand the next one. And this problem is exactly the crystallization problem.

²That is, $V \equiv +\infty$ sur $[0, 1 - \varepsilon)$, $V \equiv 0$ on $[1 + \varepsilon, \infty)$ and $\min(V) = V(1) < 0$, with small ε .

4. EXTENSIONS

4.1. Positive temperature. Until now we have only considered the problem of minimizing the energy, that is, we have assumed the temperature to be 0. As a matter of fact, it seems relevant to assume that crystallization only occurs for small temperature [140]. At positive temperature $T > 0$, the problem may be formulated in the same way, up to the fact that the point particles are replaced by a probability density on \mathbb{R}^{dN} (recall that N is the number of particles), and that an entropy term is added to the energy. In such a case, one needs to confine the system, which may be done by imposing that the particles are restricted to be in a bounded domain Ω , as in Section 3.3. Another possibility is to work in the whole space \mathbb{R}^d , and add a confining external potential V_{ext} to the energy \mathcal{E}_N , that is, a term of the form $\sum_{j=1}^N V_{\text{ext}}(x_j)$, with $V_{\text{ext}}(x) \rightarrow +\infty$ when $|x| \rightarrow +\infty$, as was done in (33). As before, the confinement in a domain Ω is equivalent to using the external confining potential

$$V_{\text{ext}}(x) = \begin{cases} 0 & \text{if } x \in \Omega, \\ +\infty & \text{otherwise.} \end{cases}$$

An advantage of this setting is that the problem becomes translation invariant in the thermodynamic limit.

Formulation. The situation is slightly simpler than in the case $T = 0$, since the minimizer of the free energy is unique and explicitly known: it is the Gibbs measure³

$$P_{\Omega, N, T}(x_1, \dots, x_N) = \frac{e^{-\frac{\mathcal{E}_N(x_1, \dots, x_N)}{T}}}{\int_{\Omega^N} e^{-\frac{\mathcal{E}_N(x_1, \dots, x_N)}{T}} dx_1 \cdots dx_N}. \quad (38)$$

This distribution concentrates on the minima of \mathcal{E}_N when $T \rightarrow 0$. This probability measure is a minimizer of the free energy

$$F_{\Omega, N, T} := \min_{\substack{P \text{ symmetric probability} \\ \text{measure on } \Omega^N}} \left\{ \int_{\Omega^N} \mathcal{E}_N(x_1, \dots, x_N) P(x_1, \dots, x_N) dx_1 \cdots dx_N + T \int_{\Omega^N} P(x_1, \dots, x_N) \log P(x_1, \dots, x_N) dx_1 \cdots dx_N \right\}, \quad (39)$$

in which the first term is the energy of the system, and the second one is the opposite of the entropy. The symmetry of P accounts for the fact that the particles are identical and indistinguishable. The solution of this problem is unique, given by (38), and satisfies $F_{\Omega, N, T} = -T \log \left(\int_{\Omega^N} e^{-\mathcal{E}_N/T} \right)$.

In order to formalize the crystallization problem at positive temperature, it is convenient to consider the limit of the *empirical measures* (also called k -point correlation functions), which are similar to the measure μ_N introduced in (10). To be more precise, we define the family of probability measures, obtained by integrating with respect to all variables except k of them:

$$\mu_{\Omega, N, T}^{(k)}(x_1, \dots, x_k) = \frac{N!}{(N-k)!} \int_{\Omega^{N-k+1}} P_{\Omega, N, T}(x_1, \dots, x_k, y_{k+1}, \dots, y_N) dy_{k+1} \cdots dy_N \quad (40)$$

and we say that crystallization occurs if all the measures $\mu_{\Omega_N, N, T}^{(k)}$ locally converge (possibly up to extraction of a subsequence) to some locally finite measures $\mu_{\rho, T}^{(k)}$ in the thermodynamic limit $N \rightarrow \infty$ with $N/|\Omega_N| \rightarrow \rho$, and if these measure are invariant under the action of a (maximal) group G :

$$\forall g \in G, \quad \mu_{\rho, T}^{(k)}(x_1 + g, \dots, x_k + g) = \mu_{\rho, T}^{(k)}(x_1, \dots, x_k).$$

Here again the limit may depend on the subsequence, or on the sequence of domains (Ω_N) . For instance, it is possible for the object obtained in the limit to be a convex combination of translates of the minimizing lattice, in which case, $\mu_{\rho, T}^{(1)}$ is a constant. In order to find the actual period of the lattice, one then needs to study $\mu_{\rho, T}^{(k)}$ for $k \geq 2$.

³It is also possible to consider the Hamiltonian (1), but the Gibbs measure $e^{-\mathcal{H}_N/T}$ can then be factorized and the variables p_i do not play any role. The situation is different in the quantum case (Section 4.3).

In the zero-temperature case, we only considered the measure $\mu^{(1)}$, which appears in (11). The reason for this is that, in such a case, the total probability is

$$P_{\Omega,N}(y_1, \dots, y_N) = \frac{1}{N!} \sum_{\sigma \in \mathfrak{S}^N} \delta_{x_{\sigma(1)}}(y_1) \cdots \delta_{x_{\sigma(N)}}(y_N)$$

where x_1, \dots, x_N is a solution to problem (2). Because of this specific form, local convergence for $k = 1$ to μ implies that all the other empirical measures $\mu_\rho^{(k)}(x_1, \dots, x_k)$ converge to $\mu(x_1) \cdots \mu(x_k)$. Such a property is unclear for $T > 0$.

Known results. Few results have been proved at positive temperature. Actually, one expects crystallization only for T small enough. In this respect, Wigner's problem described in Section 3.5 is an exception for which crystallization occurs for any T and any density ρ . This has been proved in dimension $d = 1$ [108, 31, 4]. Numerical simulations indicate that, in dimension $d \geq 2$, there exists a critical temperature T_c such that, if $T > T_c$, then Jellium is not crystallized [34, 95, 137, 78, 6, 52, 5, 167, 55, 23].

Link with random matrices. The N eigenvalues of an $N \times N$ matrix with random coefficients are, in some situation, distributed according to the Gibbs measure of a gas of particles. The effective interaction potential will usually be $V(x) = -\log|x|$, and the dimension $d = 1$ (if the eigenvalues are real) or $d = 2$ (if they are complex). If the entries of the matrix are independent Gaussian variables, the statistical distribution of the eigenvalues $\lambda_1, \dots, \lambda_N$ is given by the Gibbs measure (38) with

$$\mathcal{E}_N(\lambda_1, \dots, \lambda_N) = -\frac{1}{N} \sum_{1 \leq k < \ell \leq N} \log|\lambda_k - \lambda_\ell| + \sum_{j=1}^N |\lambda_j|^2.$$

For hermitian matrices (*GUE*, that is, *Gaussian Unitary Ensemble*), the problem is set in $\Omega = \mathbb{R}$, since the eigenvalues have no imaginary part. In such a case, the temperature is equal to $T = 1/(2N)$. If one imposes that the matrices have real coefficients (*GOE*, that is, *Gaussian Orthogonal Ensemble*), the temperature is $T = 1/N$. When considering complex matrices without any symmetry assumption (*Ginibre ensemble*), we have the same formula, but the λ_i are now in $\Omega = \mathbb{C} = \mathbb{R}^2$ and the temperature is $T = 1/(2N)$.

It is also possible to consider unitary or orthogonal matrices (*CUE* for *Circular Unitary Ensemble*, and *COE* for *Circular Orthogonal Ensemble*, respectively), using the uniform law on this compact subset of matrices. Then, the eigenvalues are distributed according to the Gibbs measure (38) with

$$\mathcal{E}_N(\lambda_1, \dots, \lambda_N) = -\frac{1}{N} \sum_{1 \leq k < \ell \leq N} \log|\lambda_k - \lambda_\ell|,$$

this time restricted to the unit circle $\Omega = S^1$.

Studying the eigenvalues of random matrices and the link with Coulomb gas is a very active subject, which started with the seminal works of E. Wigner [179, 180] and F. Dyson [56, 57, 58, 61, 126]. The interest of the set of matrices we just mentioned is that they allow for explicit computation of empirical measures, hence a good knowledge of the statistics of these eigenvalues. Since T behaves like $1/N$, the first order corresponds to the zero-temperature setting. The average distribution of the eigenvalues is given by the measure σ solution to the minimization problem in (34). The next order is more complex and its link with the crystal problem is less clear [58]. We refer for instance to [125, 72, 9] for a detailed study of the subject.

4.2. Several types of particles. In order to deal with long-range interactions (for instance Coulomb potential), as in Wigner problem presented in Section 3.5, it is possible to add a background homogeneous density making the system globally neutral. Another model, more important from a practical viewpoint, is the case of two (or more) different types of atoms or ions, with different charges. One can think for instance of sodium chloride crystal, which is made of two face centered cubic lattices, one (Na^+ ions) shifted with respect to the other (Cl^- ions).

For the sake of simplicity, let us consider only two types of particles. The interaction between two identical particles is different from the interaction between two different ones. We are thus led

to the energy

$$\begin{aligned} \mathcal{E}_{N_1, N_2}(x_1, \dots, x_{N_1}, y_1, \dots, y_{N_2}) \\ = \sum_{1 \leq i < j \leq N_1} V_{11}(|x_i - x_j|) + \sum_{1 \leq i < j \leq N_2} V_{22}(|y_i - y_j|) + \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} V_{12}(|x_i - y_j|) \end{aligned}$$

where x_i and y_i are the positions of the particles of each type. We study the limit $N_1, N_2 \rightarrow \infty$, possibly imposing a link between N_1 and N_2 , accounting for a charge difference between the two types of particles. Thinking of a 3D crystal composed of charges of opposite sign q_1 et $-q_2$, we assume that

$$V_{11}(|x|) \underset{|x| \rightarrow \infty}{\sim} \frac{q_1^2}{|x|}, \quad V_{22}(|x|) \underset{|x| \rightarrow \infty}{\sim} \frac{q_2^2}{|x|}, \quad V_{12}(|x|) \underset{|x| \rightarrow \infty}{\sim} -\frac{q_1 q_2}{|x|},$$

and we impose the neutrality condition $q_1 N_1 - q_2 N_2 \rightarrow 0$ in the limit. For such a classical model, Coulomb interaction is not adapted, since the energy tends to $-\infty$ as two particles of opposite charge get closer to each other, and the model is unstable (note, however, that it is stable in the quantum case, as it was proved by Dyson-Lenard [59, 112] and Lieb-Thirring [120]). Hence, one needs to assume that the potentials V_{11} , V_{22} and V_{12} are strongly repulsive at short distance $|x| \rightarrow 0$.

Several conjectures have been made concerning the optimal lattices [29], but we do not know any result on the crystal problem with several types of particles. Thinking of crystalline structures currently observed in nature, it is a highly important question from a physical viewpoint. A review of known results in 3D for high temperature (hence without crystallization) is given in [35]. In [139] Radin considers special short-range potentials for two types of particles, and proves that crystallization fails, but the minimizers are quasi-periodic.

4.3. Quantum models. In the classical models studied so far, the kinetic energy of the particles does not play any role, since we deal with minimizers or Gibbs states. The term $\sum_{j=1}^N |p_j|^2 / (2m)$ in (1) disappears in the minimization problem, and factors out and gives a Gaussian at positive temperature in (38). The situation is different in quantum mechanics, in which there is a link between velocity and position, in order to respect Heisenberg's uncertainty principle. This makes the kinetic energy dependent on the positions of the particles. More precisely, quantum mechanics principles imply that p_j should be replaced by the differential operator $-i\hbar \nabla_{x_j}$ and that the Hamiltonian $\mathcal{H}_N(p_1, \dots, p_N, x_1, \dots, x_N)$ in (1) should be replaced by the differential operator

$$H_N = -\sum_{j=1}^N \frac{\hbar^2}{2m} \Delta_{x_j} + \sum_{1 \leq k < \ell \leq N} V(x_k - x_\ell). \quad (41)$$

This operator acts on $L^2(\Omega^N)$, where $\Omega = \mathbb{R}^d$ for an unconfined system, and where Ω is a bounded domain if the system is confined (with suitable boundary conditions). Since the particles are indistinguishable, we work with a subspace of $L^2(\Omega^N)$ consisting of functions having a prescribed symmetry property. In nature one can find two types of particles: *bosons* and *fermions*. For bosons, we use the subspace $L_s^2(\Omega^N)$ of functions which are symmetric with respect to variable permutations. For fermions, we use the subspace $L_a^2(\Omega^N)$ of functions which are antisymmetric. Properties of the system in the limit $N \rightarrow \infty$ depend on the chosen symmetry class. For the sake of simplicity, we ignore the spin variable.

The classical problems studied so far read, in the quantum case,

$$\begin{aligned} E_{a/s, \Omega}(N) \\ = \inf_{\substack{\Psi \in L_{a/s}^2(\Omega^N) \\ \int |\Psi|^2 = 1}} \int_{\Omega^N} \left(\frac{\hbar^2}{2m} |\nabla \Psi(x_1, \dots, x_N)|^2 + \sum_{1 \leq k < \ell \leq N} V(x_k - x_\ell) |\Psi(x_1, \dots, x_N)|^2 \right) dx_1 \cdots dx_N \end{aligned} \quad (42)$$

and

$$F_{a/s, \Omega}(N) = -T \log \left(\text{tr}_{L_{a/s}^2(\Omega^N)} e^{-H_N/T} \right)$$

for the free energy (39). In the semi-classical limit $\hbar \rightarrow 0$, these energies converge (up to a constant which diverges like $\log \hbar$ for $F_{a/s, \Omega}(N)$) to the corresponding classical energies.

Quantum mechanics is by nature a probabilistic theory and the study of crystallization uses the weak limit of the empirical measures, as in the case of positive temperature classical model. For instance, one can study the limit of k -points densities

$$\mu_{\Omega,N}^{(k)}(x_1, \dots, x_k) := \frac{N!}{(N-k)!} \int_{\Omega_{N-k}} |\Psi_{\Omega,N}(x_1, \dots, x_k, y_{k+1}, \dots, y_N)|^2 dy_{k+1} \cdots dy_N$$

where $\Psi_{\Omega,N}$ is a minimizer of problem (42) (this minimizer is always unique, up to a phase, for bosons, but it is not necessarily unique for fermions). A similar formula is valid at positive temperature, expressed in terms of the Gibbs operator $Z_T^{-1} e^{-H_N/T}$, but we do not enter such details. The measure $\mu_{\Omega,N}^{(k)}$ is a classical object which does not carry all the information on the system (for instance the probability associated with the kinetic energy involves $|\widehat{\Psi}|^2$ instead of $|\Psi|^2$). It is more relevant to study the limit of k -body density operators, which are defined by their integral kernel

$$\begin{aligned} & \gamma_{\Omega,N}^{(k)}(x_1, \dots, x_k, x'_1, \dots, x'_k) \\ & := \frac{N!}{(N-k)!} \int_{\Omega_{N-k}} \Psi_{\Omega,N}(x_1, \dots, x_k, y_{k+1}, \dots, y_N) \overline{\Psi_{\Omega,N}(x'_1, \dots, x'_k, y_{k+1}, \dots, y_N)} dy_{k+1} \cdots dy_N, \end{aligned} \quad (43)$$

which diagonal part coincides with $\mu_{\Omega,N}^{(k)}$. We say that the system crystallizes if these operators locally converge to operators $\gamma^{(k)}$ which commute with translations of a (maximal) lattice G , that is,

$$\forall g \in G, \quad \gamma_{\Omega,N}^{(k)}(x_1 + g, \dots, x_k + g, x'_1 + g, \dots, x'_k + g) = \gamma_{\Omega,N}^{(k)}(x_1, \dots, x_k, x'_1, \dots, x'_k).$$

Few results have been proved for the crystal problem in the case of continuum quantum systems. In particular, one could think that, when a classical system exhibits crystallization, so does the quantum corresponding system if \hbar is sufficiently small. This has not been studied, to our knowledge, except in the case of Coulomb gas (quantum Jellium) for which Kunz [108] and Brascamp-Lieb [31] have proved crystallization for small density ρ in dimension $d = 1$. After a change of scale, assuming that ρ is small is equivalent to assuming \hbar is small, so the situation is indeed a semi-classical limit. Crystallization for 1D quantum Jellium (at any density ρ and any temperature T) has been recently proved by Jansen and Jung [99].

Some results have been proved for quantum systems described by nonlinear models, such as Thomas-Fermi or Hartree. Assuming that the nuclei are classical particles with positive charge and are distributed on a lattice, it has been proved for convex models that the electrons are periodically arranged [119, 41, 42, 43, 39]. If in addition one optimizes over the positions of the nuclei, then crystallization is only known in 1D for Thomas-Fermi type models [20].

4.4. Discrete systems. In our review, we focused on continuous systems, defined in the whole space or in a domain Ω_N which grows as $N \rightarrow +\infty$. An important literature is devoted to the study of *discrete systems*. Such systems are defined on a lattice $G \subset \mathbb{R}^d$, without assuming *a priori* that the corresponding states are G -periodic. We expect that proving that the system is periodic is easier, since a natural periodic lattice is already present in the definition of the system. Many rigorous results have been proved for this kind of problems, although important questions are still unsolved. The models considered can be either quantum or classical.

Examples of such systems are the (classical or quantum) Heisenberg or Ising models. Two main regimes are usually dealt with: the ferromagnetic one, in which spins tend to be aligned with each other, and antiferromagnetic in which spins are preferably of alternate sign. In this latter case, crystallization gives a periodic lattice which size is twice that of the original one.

In 1986, Kennedy and Lieb have considered two systems of this type. In [101, 102, 114], they study electrons on a lattice, submitted to a pointwise interaction with fixed particles of opposite spin. They prove that the electrons are located on a sub-lattice. In [103] they consider a 1D system on the lattice \mathbb{Z} . This model describes for instance deformations of a polyacetylene molecule. They prove that the minimizer is periodic of period 2, a phenomenon called *Peierls instability*. This result has been further developed in [116, 115, 117]. It has been generalized in [79], and extended to the hexagonal lattice in 2D in [73].

Apart from systems with analytical solutions, an important method for studying classical or quantum spin systems is the *reflection positivity* method. This strategy has been introduced in field theory [135], then adapted and developed in the case of spin systems [77, 60, 76, 74, 75].

This method aims at proving phase transitions and long-range order. However, it does not always allow to conclude that the system is periodic. For recent examples of application of this theory to crystallization problems, see for instance [82, 83, 85, 86].

CONCLUSION

We have described several aspects of an important problem arising in physics and which, in spite of an intense activity, is still not completely understood mathematically. In addition to the famous crystallization problem, several questions have been reported on, some of which are probably more at hand than others. Some progress in any of these directions would be of high interest and would improve the theoretical understanding of the structure of matter at the microscopic scale. We hope that this article will stimulate further research in these directions.

REFERENCES

- [1] J. R. ABO-SHAEER, C. RAMAN, J. M. VOGELS, AND W. KETTERLE, *Observation of vortex lattices in Bose-Einstein condensates*, Science, 292 (2001), pp. 476–479.
- [2] A. ABRIKOSOV, *The magnetic properties of superconducting alloys*, J. Phys. Chem. Solids, 2 (1957), pp. 199 – 208.
- [3] A. AFTALION, X. BLANC, AND F. NIER, *Lowest Landau level functional and Bargmann spaces for Bose-Einstein condensates*, J. Funct. Anal., 241 (2006), pp. 661–702.
- [4] M. AIZENMAN AND P. A. MARTIN, *Structure of Gibbs states of one dimensional Coulomb systems*, Comm. Math. Phys., 78 (1980), pp. 99–116.
- [5] A. ALASTUEY, *Propriétés d'équilibre du plasma classique à une composante en trois et deux dimensions*, Ann. Phys. Fr., 11 (1986), pp. 653–738.
- [6] A. ALASTUEY AND B. JANCOVICI, *On the classical two-dimensional one-component Coulomb plasma*, J. Phys. France, 42 (1981), pp. 1–12.
- [7] G. ALBERTI, R. CHOKSI, AND F. OTTO, *Uniform energy distribution for an isoperimetric problem with long-range interactions*, J. Amer. Math. Soc., 22 (2009), pp. 569–605.
- [8] G. ALBERTI AND S. MÜLLER, *A new approach to variational problems with multiple scales*, Comm. Pure Appl. Math., 54 (2001), pp. 761–825.
- [9] G. W. ANDERSON, A. GUIONNET, AND O. ZEITOUNI, *An introduction to random matrices*, vol. 118 of Cambridge Studies in Advanced Mathematics, Cambridge University Press, Cambridge, 2010.
- [10] X. ANTOINE AND R. DUBOSCQ, *GPELab, a Matlab toolbox to solve Gross-Pitaevskii equations I: Computation of stationary solutions*, Comput. Phys. Commun., 185 (2014), pp. 2969 – 2991.
- [11] X. ANTOINE AND R. DUBOSCQ, *Robust and efficient preconditioned Krylov spectral solvers for computing the ground states of fast rotating and strongly interacting Bose-Einstein condensates*, J. Comput. Phys., 258 (2014), pp. 509–523.
- [12] N. ASHCROFT AND N. MERMIN, *Solid State Physics*, Saunders, Philadelphia, 1976.
- [13] Y. AU YEUNG, G. FRIESECKE, AND B. SCHMIDT, *Minimizing atomic configurations of short range pair potentials in two dimensions: crystallization in the Wulff shape*, Calc. Var. Partial Differential Equations, 44 (2012), pp. 81–100.
- [14] A. BEN HAJ YEDDER, X. BLANC, AND C. LE BRIS, *A numerical investigation of the 2-dimensional crystal problem*, Tech. Rep. R03003, Laboratoire J.-L. Lions, Université Pierre et Marie Curie, 2003.
- [15] L. BÉTERMIN, *2D Theta Functions and Crystallization among Bravais Lattices*, ArXiv e-prints, (2015).
- [16] L. BÉTERMIN AND P. ZHANG, *Minimization of energy per particle among Bravais lattices in \mathbb{R}^2 : Lennard-Jones and Thomas-Fermi cases*, Commun. Contemp. Math., (2014).
- [17] F. BETHUEL, H. BREZIS, AND F. HÉLEIN, *Ginzburg-Landau vortices*, Progress in Nonlinear Differential Equations and their Applications, 13, Birkhäuser Boston, Inc., Boston, MA, 1994.
- [18] F. BETHUEL AND T. RIVIÈRE, *Vortices for a variational problem related to superconductivity*, Ann. Inst. H. Poincaré Anal. Non Linéaire, 12 (1995), pp. 243–303.
- [19] X. BLANC, *Lower bound for the interatomic distance in Lennard-Jones clusters*, Comput. Optim. Appl., 29 (2004), pp. 5–12.
- [20] X. BLANC AND C. L. BRIS, *Periodicity of the infinite-volume ground state of a one-dimensional quantum model*, Nonlinear Anal., 48 (2002), pp. 791–803.
- [21] T. BODINEAU, *The Wulff construction in three and more dimensions*, Comm. Math. Phys., 207 (1999), pp. 197–229.
- [22] T. BODINEAU, D. IOFFE, AND Y. VELENIK, *Rigorous probabilistic analysis of equilibrium crystal shapes*, J. Math. Phys., 41 (2000), pp. 1033–1098. Probabilistic techniques in equilibrium and nonequilibrium statistical physics.
- [23] M. BONITZ, P. LUDWIG, H. BAUMGARTNER, C. HENNING, A. FILINOV, D. BLOCK, O. ARP, A. PIEL, S. KÄDING, Y. IVANOV, A. MELZER, H. FEHSKE, AND V. FILINOV, *Classical and quantum coulomb crystals*, Physics of Plasmas (1994-present), 15 (2008), pp. –.
- [24] L. BONSALL AND A. A. MARADUDIN, *Some static and dynamical properties of a two-dimensional Wigner crystal*, Phys. Rev. B, 15 (1977), pp. 1959–1973.

- [25] S. V. BORODACHOV, *Lower order terms of the discrete minimal Riesz energy on smooth closed curves*, *Canad. J. Math.*, 64 (2012), pp. 24–43.
- [26] D. BORWEIN, J. M. BORWEIN, AND R. SHAIL, *Analysis of certain lattice sums*, *J. Math. Anal. Appl.*, 143 (1989), pp. 126–137.
- [27] D. BORWEIN, J. M. BORWEIN, R. SHAIL, AND I. J. ZUCKER, *Energy of static electron lattices*, *J. Phys. A*, 21 (1988), pp. 1519–1531.
- [28] D. BORWEIN, J. M. BORWEIN, AND A. STRAUB, *On lattice sums and Wigner limits*, *J. Math. Anal. Appl.*, 414 (2014), pp. 489–513.
- [29] J. M. BORWEIN, M. L. GLASSER, R. C. MCPHEDRAN, J. G. WAN, AND I. J. ZUCKER, *Lattice sums then and now*, vol. 150 of *Encyclopedia of Mathematics and its Applications*, Cambridge University Press, Cambridge, 2013. With a foreword by Helaman Ferguson and Claire Ferguson.
- [30] D. P. BOURNE, M. A. PELETIER, AND F. THEIL, *Optimality of the triangular lattice for a particle system with Wasserstein interaction*, *Comm. Math. Phys.*, 329 (2014), pp. 117–140.
- [31] H. J. BRASCAMP AND E. H. LIEB, *Some inequalities for gaussian measures and the long-range order of the one-dimensional plasma*, in *Functional Integration and Its Applications*, A. Arthurs, ed., Oxford, 1975, Clarendon Press.
- [32] J. S. BRAUCHART, *About the second term of the asymptotics for optimal Riesz energy on the sphere in the potential-theoretical case*, *Integral Transforms Spec. Funct.*, 17 (2006), pp. 321–328.
- [33] J. S. BRAUCHART, D. P. HARDIN, AND E. B. SAFF, *The next-order term for optimal Riesz and logarithmic energy asymptotics on the sphere*, in *Recent advances in orthogonal polynomials, special functions, and their applications*, vol. 578 of *Contemp. Math.*, Amer. Math. Soc., Providence, RI, 2012, pp. 31–61.
- [34] S. G. BRUSH, H. L. SAHLIN, AND E. TELLER, *Monte carlo study of a one-component plasma. i*, *The Journal of Chemical Physics*, 45 (1966), pp. 2102–2118.
- [35] D. C. BRYDGES AND P. A. MARTIN, *Coulomb systems at low density: A review*, *Journal of Statistical Physics*, 96 (1999), pp. 1163–1330.
- [36] L. BÉTERMIN, *Renormalized Energy and Asymptotic Expansion of Optimal Logarithmic Energy on the Sphere*, *ArXiv e-prints*, (2014).
- [37] E. CAGLIOTI, P.-L. LIONS, C. MARCHIORO, AND M. PULVIRENTI, *A special class of stationary flows for two-dimensional Euler equations: a statistical mechanics description*, *Comm. Math. Phys.*, 143 (1992), pp. 501–525.
- [38] ———, *A special class of stationary flows for two-dimensional Euler equations: a statistical mechanics description. II*, *Comm. Math. Phys.*, 174 (1995), pp. 229–260.
- [39] É. CANGÈS, A. DELEURENCE, AND M. LEWIN, *A new approach to the modelling of local defects in crystals: the reduced Hartree-Fock case*, *Commun. Math. Phys.*, 281 (2008), pp. 129–177.
- [40] J. W. S. CASSELS, *On a problem of Rankin about the Epstein zeta-function*, *Proc. Glasgow Math. Assoc.*, 4 (1959), pp. 73–80.
- [41] I. CATTO, C. LE BRIS, AND P.-L. LIONS, *The mathematical theory of thermodynamic limits: Thomas-Fermi type models*, *Oxford Mathematical Monographs*, The Clarendon Press Oxford University Press, New York, 1998.
- [42] ———, *On the thermodynamic limit for Hartree-Fock type models*, *Ann. Inst. H. Poincaré Anal. Non Linéaire*, 18 (2001), pp. 687–760.
- [43] I. CATTO, C. LE BRIS, AND P.-L. LIONS, *On some periodic Hartree-type models for crystals*, *Ann. Inst. H. Poincaré Anal. Non Linéaire*, 19 (2002), pp. 143–190.
- [44] R. CERF AND Á. PISZTORA, *On the Wulff crystal in the Ising model*, *Ann. Probab.*, 28 (2000), pp. 947–1017.
- [45] X. CHEN AND Y. OSHITA, *Periodicity and uniqueness of global minimizers of an energy functional containing a long-range interaction*, *SIAM J. Math. Anal.*, 37 (2005), pp. 1299–1332 (electronic).
- [46] R. CHOKSI AND M. A. PELETIER, *Small volume fraction limit of the diblock copolymer problem: I. Sharp-interface functional*, *SIAM J. Math. Anal.*, 42 (2010), pp. 1334–1370.
- [47] G. CHOQUET, *Diamètre transfini et comparaison de diverses capacités*, in *Séminaire Brelot-Choquet-Deny. Théorie du potentiel*, 1958-1959. Exp. 4.
- [48] H. COHN AND A. KUMAR, *Universally optimal distribution of points on spheres*, *J. Amer. Math. Soc.*, 20 (2007), pp. 99–148.
- [49] J. H. CONWAY AND N. J. A. SLOANE, *Sphere packings, lattices and groups*, vol. 290 of *Grundlehren der Mathematischen Wissenschaften [Fundamental Principles of Mathematical Sciences]*, Springer-Verlag, New York, third ed., 1999. With additional contributions by E. Bannai, R. E. Borcherds, J. Leech, S. P. Norton, A. M. Odlyzko, R. A. Parker, L. Queen and B. B. Venkov.
- [50] R. COULANGEON, *Spherical designs and zeta functions of lattices*, *Int. Math. Res. Not.*, (2006), pp. Art. ID 49620, 16.
- [51] R. COULANGEON AND A. SCHÜRMAN, *Energy minimization, periodic sets and spherical designs*, *Int. Math. Res. Not. IMRN*, (2012), pp. 829–848.
- [52] S. DE LEEUW AND J. PERRAM, *Statistical mechanics of two-dimensional Coulomb systems: II. the two-dimensional one-component plasma*, *Physica A: Statistical Mechanics and its Applications*, 113 (1982), pp. 546–558.
- [53] P. H. DIANANDA, *Notes on two lemmas concerning the Epstein zeta-function*, *Proc. Glasgow Math. Assoc.*, 6 (1964), pp. 202–204.

- [54] A. D. DINSMORE, M. F. HSU, M. G. NIKOLAIDES, M. MARQUEZ, A. R. BAUSCH, AND D. A. WEITZ, *Colloidosomes: Selectively permeable capsules composed of colloidal particles*, Science, 298 (2002), pp. 1006–1009.
- [55] D. H. E. DUBIN AND T. M. O’NEIL, *Trapped nonneutral plasmas, liquids, and crystals (the thermal equilibrium states)*, Rev. Mod. Phys., 71 (1999), pp. 87–172.
- [56] F. J. DYSON, *Statistical theory of the energy levels of complex systems. I*, J. Math. Phys., 3 (1962), pp. 140–156.
- [57] ———, *Statistical theory of the energy levels of complex systems. II*, J. Math. Phys., 3 (1962), pp. 157–165.
- [58] ———, *Statistical theory of the energy levels of complex systems. III*, J. Math. Phys., 3 (1962), pp. 166–175.
- [59] F. J. DYSON AND A. LENARD, *Stability of matter. I*, J. Math. Phys., 8 (1967), pp. 423–434.
- [60] F. J. DYSON, E. H. LIEB, AND B. SIMON, *Phase transitions in quantum spin systems with isotropic and nonisotropic interactions*, J. Stat. Phys., 18 (1978), pp. 335–383.
- [61] F. J. DYSON AND M. L. MEHTA, *Statistical theory of the energy levels of complex systems. IV*, J. Math. Phys., 4 (1963), pp. 701–712.
- [62] W. E AND D. LI, *On the crystallization of 2D hexagonal lattices*, Comm. Math. Phys., 286 (2009), pp. 1099–1140.
- [63] V. ENNOLA, *A lemma about the Epstein zeta-function*, Proc. Glasgow Math. Assoc., 6 (1964), pp. 198–201.
- [64] V. ENNOLA, *On a problem about the Epstein zeta-function*, Proc. Cambridge Philos. Soc., 60 (1964), pp. 855–875.
- [65] P. EPSTEIN, *Zur Theorie allgemeiner Zetafunktionen. II*, Math. Ann., 63 (1906), pp. 205–216.
- [66] P. P. EWALD, *Die berechnung optischer und elektrostatischer gitterpotentiale*, Ann. Phys., 369 (1921), pp. 253–287.
- [67] K. FIELDS, *Locally minimal Epstein zeta functions*, Mathematika, 27 (1980), pp. 17–24.
- [68] M. E. FISHER, *The free energy of a macroscopic system*, Arch. Ration. Mech. Anal., 17 (1964), pp. 377–410.
- [69] M. E. FISHER AND D. RUELLE, *The stability of many-particle systems*, J. Math. Phys., 7 (1966), pp. 260–270.
- [70] L. FLATLEY AND F. THEIL, *Face-centered cubic crystallization of atomistic configurations*, arXiv eprints, (2013).
- [71] FLYSPECK TEAM, *Announcement of completion of the flyspeck project*. <https://code.google.com/p/flyspeck/wiki/AnnouncingCompletion>, august 2014.
- [72] P. J. FORRESTER, *Log-gases and random matrices*, vol. 34 of London Mathematical Society Monographs Series, Princeton University Press, Princeton, NJ, 2010.
- [73] R. L. FRANK AND E. H. LIEB, *Possible lattice distortions in the Hubbard model for graphene*, Phys. Rev. Lett., 107 (2011), p. 066801.
- [74] J. FRÖHLICH, R. B. ISRAEL, E. H. LIEB, AND B. SIMON, *Phase transitions and reflection positivity. i. general theory and long range lattice models*, Comm. Math. Phys., 62 (1978), pp. 1–34.
- [75] ———, *Phase transitions and reflection positivity. ii. lattice systems with short-range and Coulomb interactions*, J. Stat. Phys., 22 (1980), pp. 297–347.
- [76] J. FRÖHLICH AND E. H. LIEB, *Phase transitions in anisotropic lattice spin systems*, Communications in Mathematical Physics, 60 (1978), pp. 233–267.
- [77] J. FRÖHLICH, B. SIMON, AND T. SPENCER, *Infrared bounds, phase transitions and continuous symmetry breaking*, Comm. Math. Phys., 50 (1976), pp. 79–95.
- [78] R. GANN, S. CHAKRAVARTY, AND G. CHESTER, *Monte carlo simulation of the classical two-dimensional one-component plasma*, Phys. Rev. B, 20 (1979), pp. 326–344.
- [79] M. GARCIA ARROYO AND E. SÉRÉ, *Existence of kink solutions in a discrete model of the polyacetylene molecule*. Preprint hal-00769075, Dec. 2012.
- [80] C. S. GARDNER AND C. RADIN, *The infinite-volume ground state of the Lennard-Jones potential*, J. Statist. Phys., 20 (1979), pp. 719–724.
- [81] C. F. GAUSS, *Untersuchungen über die Eigenschaften der positiven ternären quadratischen Formen von Ludwig August Seeber*, J. Reine. Angew. Math, 20 (1840), pp. 312–320.
- [82] A. GIULIANI, J. L. LEBOWITZ, AND E. H. LIEB, *Ising models with long-range antiferromagnetic and short-range ferromagnetic interactions*, Phys. Rev. B, 74 (2006), p. 064420.
- [83] ———, *Striped phases in two-dimensional dipole systems*, Phys. Rev. B, 76 (2007), p. 184426.
- [84] ———, *Periodic minimizers in 1d local mean field theory*, Comm. Math. Phys., 286 (2009), pp. 163–177.
- [85] A. GIULIANI, E. H. LIEB, AND R. SEIRINGER, *Realization of stripes and slabs in two and three dimensions*, Phys. Rev. B, 88 (2013), p. 064401.
- [86] ———, *Formation of stripes and slabs near the ferromagnetic transition*, Comm. Math. Phys., 331 (2014), pp. 333–350.
- [87] G. GIULIANI AND G. VIGNALE, *Quantum Theory of the Electron Liquid*, Cambridge University Press, 2005.
- [88] L. GLASSER AND A. G. EVERY, *Energies and spacings of point charges on a sphere*, J. Phys. A, Math. Gen., 25 (1992), p. 2473.
- [89] D. GOLDMAN, C. B. MURATOV, AND S. SERFATY, *The Γ -limit of the two-dimensional Ohta-Kawasaki energy. I. Droplet density*, Arch. Ration. Mech. Anal., 210 (2013), pp. 581–613.
- [90] ———, *The Γ -limit of the two-dimensional Ohta-Kawasaki energy. Droplet arrangement via the renormalized energy*, Arch. Ration. Mech. Anal., 212 (2014), pp. 445–501.
- [91] P. M. GRUBER, *Application of an idea of Voronoï to lattice zeta functions*, Proc. Steklov Inst. Math., 276 (2012), pp. 103–124.

- [92] M. GÖTZ AND E. B. SAFF, *Note on d -extremal configurations for the sphere in \mathbb{R}^{d+1}* , in Recent Progress in Multivariate Approximation, W. Haussmann, K. Jetter, and M. Reimer, eds., vol. 137 of ISNM International Series of Numerical Mathematics, Birkhäuser Basel, 2001, pp. 159–162.
- [93] T. C. HALES, *A proof of the Kepler conjecture*, Ann. of Math. (2), 162 (2005), pp. 1065–1185.
- [94] G. C. HAMRICK AND C. RADIN, *The symmetry of ground states under perturbation*, J. Statist. Phys., 21 (1979), pp. 601–607.
- [95] J. HANSEN, *Statistical mechanics of dense ionized matter. i. equilibrium properties of the classical one-component plasma*, Phys. Rev. A, 8 (1973), pp. 3096–3109.
- [96] D. P. HARDIN AND E. B. SAFF, *Discretizing manifolds via minimum energy points*, Notices of the AMS, 51 (2004), pp. 1186–1194.
- [97] ———, *Minimal Riesz energy point configurations for rectifiable d -dimensional manifolds*, Adv. Math., 193 (2005), pp. 174–204.
- [98] R. C. HEITMANN AND C. RADIN, *The ground state for sticky disks*, J. Statist. Phys., 22 (1980), pp. 281–287.
- [99] S. JANSEN AND P. JUNG, *Wigner crystallization in the quantum 1d jellium at all densities*, Comm. Math. Phys., (2014), pp. 1–22.
- [100] R. L. JERRARD, *Lower bounds for generalized Ginzburg-Landau functionals*, SIAM J. Math. Anal., 30 (1999), pp. 721–746.
- [101] T. KENNEDY AND E. H. LIEB, *A model for crystallization: A variation on the Hubbard model*, in Statistical Mechanics and Field Theory: Mathematical Aspects, T. C. Dorlas, N. M. Hugenholtz, and M. Winnink, eds., vol. 257 of Lecture Notes in Physics, Berlin Springer Verlag, 1986, pp. 1–9.
- [102] T. KENNEDY AND E. H. LIEB, *An itinerant electron model with crystalline or magnetic long range order*, Phys. A, 138 (1986), pp. 320 – 358.
- [103] T. KENNEDY AND E. H. LIEB, *Proof of the Peierls instability in one dimension*, Phys. Rev. Lett., 59 (1987), pp. 1309–1312.
- [104] M. K.-H. KIESSLING, *Statistical mechanics of classical particles with logarithmic interactions*, Comm. Pure. Appl. Math., 46 (1993), pp. 27–56.
- [105] M. K.-H. KIESSLING, *A note on classical ground state energies*, J. Stat. Phys., 136 (2009), pp. 275–284.
- [106] C. KITTEL, *Quantum Theory of Solids*, John Wiley & Sons, 2nd ed., 1987.
- [107] A. B. J. KUIJLAARS AND E. B. SAFF, *Asymptotics for minimal discrete energy on the sphere*, Trans. Amer. Math. Soc., 350 (1998), pp. 523–538.
- [108] H. KUNZ, *The one-dimensional classical electron gas*, Ann. Phys. (NY), 85 (1974), pp. 303 – 335.
- [109] N. S. LANDKOF, *Foundations of modern potential theory*, Springer-Verlag, New York-Heidelberg, 1972. Translated from the Russian by A. P. Doohovskoy, Die Grundlehren der mathematischen Wissenschaften, Band 180.
- [110] O. E. LANFORD, *Entropy and equilibrium states in classical statistical mechanics*, in Statistical Mechanics and Mathematical Problems, A. Lenard, ed., vol. 20 of Lecture Notes in Physics, Springer Berlin Heidelberg, 1973, pp. 1–113.
- [111] T. LEBLÉ, *A Uniqueness Result for Minimizers of the 1D Log-gas Renormalized Energy*, ArXiv e-prints, (2014).
- [112] A. LENARD AND F. J. DYSON, *Stability of matter. II*, J. Math. Phys., 9 (1968), pp. 698–711.
- [113] M. LEWIN AND E. H. LIEB, *Improved Lieb-Oxford exchange-correlation inequality with gradient correction*, Phys. Rev. A, 91 (2015), p. 022507.
- [114] E. H. LIEB, *A model for crystallization: A variation on the Hubbard model*, Phys. A, 140 (1986), pp. 240 – 250.
- [115] E. H. LIEB AND B. NACHTERGAELE, *Dimerization in ring-shaped molecules: the stability of the Peierls instability*, in XIth International Congress of Mathematical Physics (Paris, 1994), Int. Press, Cambridge, MA, 1995, pp. 423–431.
- [116] ———, *Stability of the Peierls instability for ring-shaped molecules*, Phys. Rev. B, 51 (1995), p. 4777.
- [117] ———, *Bond alternation in ring-shaped molecules: The stability of the Peierls instability*, Int. J. Quantum Chemistry, 58 (1996), pp. 699–706.
- [118] E. H. LIEB AND H. NARNHOFER, *The thermodynamic limit for jellium*, J. Stat. Phys., 12 (1975), pp. 465–465.
- [119] E. H. LIEB AND B. SIMON, *The Thomas-Fermi theory of atoms, molecules and solids*, Adv. Math., 23 (1977), pp. 22–116.
- [120] E. H. LIEB AND W. E. THIRRING, *Bound on kinetic energy of fermions which proves stability of matter*, Phys. Rev. Lett., 35 (1975), pp. 687–689.
- [121] S. C. LIM AND L. P. TEO, *On the minima and convexity of Epstein zeta function*, J. Math. Phys., 49 (2008).
- [122] E. MAININI, P. PIOVANO, AND U. STEFANELLI, *Finite crystallization in the square lattice*, Nonlinearity, 27 (2014), pp. 717–737.
- [123] E. MAININI AND U. STEFANELLI, *Crystallization in carbon nanostructures*, Comm. Math. Phys., 328 (2014), pp. 545–571.
- [124] A. MARTÍNEZ-FINKELSHTEIN, V. MAYMESKUL, E. A. RAKHMANOV, AND E. B. SAFF, *Asymptotics for minimal discrete Riesz energy on curves in \mathbb{R}^d* , Canad. J. Math., 56 (2004), pp. 529–552.
- [125] M. L. MEHTA, *Random matrices*, vol. 142 of Pure and Applied Mathematics (Amsterdam), Elsevier/Academic Press, Amsterdam, third ed., 2004.
- [126] M. L. MEHTA AND F. J. DYSON, *Statistical theory of the energy levels of complex systems. V*, J. Mathematical Phys., 4 (1963), pp. 713–719.
- [127] J. MESSER AND H. SPOHN, *Statistical mechanics of the isothermal Lane-Emden equation*, J. Statist. Phys., 29 (1982), pp. 561–578.

- [128] H. L. MONTGOMERY, *Minimal theta functions*, Glasgow Math. J., 30 (1988), pp. 75–85.
- [129] S. MÜLLER, *Singular perturbations as a selection criterion for periodic minimizing sequences*, Calc. Var. Partial Differential Equations, 1 (1993), pp. 169–204.
- [130] D. J. NEWMAN, *The hexagon theorem*, IEEE Trans. Inform. Theory, 28 (1982), pp. 137–139.
- [131] S. NONNENMACHER AND A. VOROS, *Chaotic eigenfunctions in phase space*, J. Stat. Phys., 92 (1998), pp. 431–518.
- [132] T. OHTA AND K. KAWASAKI, *Equilibrium morphology of block copolymer melts*, Macromolecules, 19 (1986), pp. 2621–2632.
- [133] L. ONSAGER, *Electrostatic interaction of molecules*, J. Phys. Chem., 43 (1939), pp. 189–196.
- [134] B. OSGOOD, R. PHILLIPS, AND P. SARNAK, *Extremals of determinants of Laplacians*, J. Funct. Anal., 80 (1988), pp. 148–211.
- [135] K. OSTERWALDER AND R. SCHRADER, *Axioms for euclidean Green's functions*, Comm. Math. Phys., 31 (1973), pp. 83–112.
- [136] M. PETRACHE AND S. SERFATY, *Next Order Asymptotics and Renormalized Energy for Riesz Interactions*, ArXiv e-prints, (2014).
- [137] E. POLLOCK AND J. HANSEN, *Statistical mechanics of dense ionized matter. ii. equilibrium properties and melting transition of the crystallized one-component plasma*, Phys. Rev. A, 8 (1973), pp. 3110–3122.
- [138] C. RADIN, *The ground state for soft disks*, J. Statist. Phys., 26 (1981), pp. 365–373.
- [139] ———, *Crystals and quasicrystals: a continuum model*, Comm. Math. Phys., 105 (1986), pp. 385–390.
- [140] ———, *Low temperature and the origin of crystalline symmetry*, Internat. J. Modern Phys. B, 1 (1987), pp. 1157–1191.
- [141] E. A. RAKHMANOV, E. B. SAFF, AND Y. M. ZHOU, *Minimal discrete energy on the sphere*, Math. Res. Lett., 1 (1994), pp. 647–662.
- [142] R. A. RANKIN, *A minimum problem for the Epstein zeta-function*, Proc. Glasgow Math. Assoc., 1 (1953), pp. 149–158.
- [143] X. REN AND J. WEI, *On energy minimizers of the diblock copolymer problem*, Interfaces Free Bound., 5 (2003), pp. 193–238.
- [144] C. A. ROGERS, *Packing and covering*, Cambridge Tracts in Mathematics and Mathematical Physics, No. 54, Cambridge University Press, New York, 1964.
- [145] S. ROTA NODARI AND S. SERFATY, *Renormalized energy equidistribution and local charge balance in 2d Coulomb system*, Int. Math. Res. Not.(IMRN), online first (2014). hal-00843427.
- [146] N. ROUGERIE, *Théorèmes de de Finetti, limites de champ moyen et condensation de Bose-Einstein*. Lecture notes, 2014.
- [147] N. ROUGERIE AND S. SERFATY, *Higher Dimensional Coulomb Gases and Renormalized Energy Functionals*, Comm. Pure Appl. Math., in press (2014).
- [148] D. RUELLE, *Classical statistical mechanics of a system of particles*, Helv. Phys. Acta, 36 (1963), pp. 183–197.
- [149] D. RUELLE, *Statistical mechanics of quantum systems of particles*, Helv. Phys. Acta, 36 (1963), pp. 789–799.
- [150] D. RUELLE, *Statistical mechanics. Rigorous results*, Singapore: World Scientific. London: Imperial College Press, 1999.
- [151] S. S. RYŠKOV, *On the question of the final ζ -optimality of lattices that yield the densest packing of n -dimensional balls*, Siberian Math. J., 14 (1973), pp. 743–750.
- [152] E. B. SAFF AND V. TOTIK, *Logarithmic potentials with external fields*, vol. 316 of Grundlehren der Mathematischen Wissenschaften [Fundamental Principles of Mathematical Sciences], Springer-Verlag, Berlin, 1997. Appendix B by Thomas Bloom.
- [153] E. SANDIER, *Lower bounds for the energy of unit vector fields and applications*, J. Funct. Anal., 152 (1998), pp. 379–403.
- [154] E. SANDIER AND S. SERFATY, *Vortices in the magnetic Ginzburg-Landau model*, Progress in Nonlinear Differential Equations and their Applications, 70, Birkhäuser Boston, Inc., Boston, MA, 2007.
- [155] ———, *From the Ginzburg-Landau model to vortex lattice problems*, Commun. Math. Phys., 313 (2012), pp. 635–743.
- [156] ———, *1d log gases and the renormalized energy: crystallization at vanishing temperature*, Probab. Theory Related Fields, (2014), pp. 1–52.
- [157] E. SANDIER AND S. SERFATY, *2D Coulomb Gases and the Renormalized Energy*, Annals of Proba., (2014).
- [158] P. SARNAK, *Determinants of Laplacians; heights and finiteness*, in Analysis, et cetera, Academic Press, Boston, MA, 1990, pp. 601–622.
- [159] P. SARNAK AND A. STRÖMBERGSSON, *Minima of Epstein's zeta function and heights of flat tori*, Invent. Math., 165 (2006), pp. 115–151.
- [160] B. SCHMIDT, *Ground states of the 2D sticky disc model: fine properties and $N^{3/4}$ law for the deviation from the asymptotic Wulff shape*, J. Stat. Phys., 153 (2013), pp. 727–738.
- [161] S. SERFATY, *Local minimizers for the Ginzburg-Landau energy near critical magnetic field. I*, Commun. Contemp. Math., 1 (1999), pp. 213–254.
- [162] ———, *Stable configurations in superconductivity: uniqueness, multiplicity, and vortex-nucleation*, Arch. Ration. Mech. Anal., 149 (1999), pp. 329–365.
- [163] ———, *Ginzburg-Landau vortices, Coulomb gases, and renormalized energies*, J. Stat. Phys., 154 (2014), pp. 660–680.
- [164] M. SKOGE, A. DONEV, F. STILLINGER, AND S. TORQUATO, *Packing hyperspheres in high-dimensional euclidean spaces*, Phys. Rev. E, 74 (2006), p. 041127.

- [165] S. SMALE, *Mathematical problems for the next century*, Math. Intell., 20 (1998), pp. 7–15.
- [166] S. L. SOBOLEV, *Formulas for mechanical cubatures in n -dimensional space*, Dokl. Akad. Nauk SSSR, 137 (1961), pp. 527–530.
- [167] S. STISHOV, *Does the phase transition exist in the one-component plasma model?*, J. Exp. Theor. Phys., 67 (1998), pp. 90–94.
- [168] F. THEIL, *A proof of crystallization in two dimensions*, Commun. Math. Phys., 262 (2006), pp. 209–236.
- [169] J. THOMSON, *Xiv. on the structure of the atom: an investigation of the stability and periods of oscillation of a number of corpuscles arranged at equal intervals around the circumference of a circle; with application of the results to the theory of atomic structure*, Philos. Mag., 7 (1904), pp. 237–265.
- [170] S. TORQUATO AND F. STILLINGER, *Exactly solvable disordered sphere-packing model in arbitrary-dimensional euclidean spaces*, Phys. Rev. E, 73 (2006), p. 031106.
- [171] S. TORQUATO AND F. H. STILLINGER, *New conjectural lower bounds on the optimal density of sphere packings*, Experimental Mathematics, 15 (2006), pp. 307–331.
- [172] UNESCO. <http://www.iycr2014.org/>, 2014. International Year of Crystallography.
- [173] W. VENTEVOGEL, *On the configuration of a one-dimensional system of interacting particles with minimum potential energy per particle*, Phys. A, 92 (1978), pp. 343 – 361.
- [174] W. J. VENTEVOGEL AND B. R. A. NIJBOER, *On the configuration of systems of interacting particles with minimum potential energy per particle*, Phys. A, 99 (1979), pp. 569–580.
- [175] ———, *On the configuration of systems of interacting particles with minimum potential energy per particle*, Phys. A, 98 (1979), pp. 274–288.
- [176] G. WAGNER, *On means of distances on the surface of a sphere (lower bounds)*, Pacific J. Math., 144 (1990), pp. 389–398.
- [177] ———, *On means of distances on the surface of a sphere. II. Upper bounds*, Pacific J. Math., 154 (1992), pp. 381–396.
- [178] E. P. WIGNER, *On the interaction of electrons in metals*, Phys. Rev., 46 (1934), pp. 1002–1011.
- [179] ———, *Characteristic vectors of bordered matrices with infinite dimensions*, Ann. of Math., 62 (1955), pp. 548–564.
- [180] ———, *Random matrices in physics*, SIAM Review, 9 (1967), pp. 1–23.
- [181] G. WULFF, *Zur Frage der Geschwindigkeit des Wachstums und der Auflösung der Krystallflächen*, Z. Kristallogr., 34 (1901), pp. 449–530.
- [182] G. L. XUE, *Minimum inter-particle distance at global minimizers of Lennard-Jones clusters*, J. Global Optim., 11 (1997), pp. 83–90.
- [183] N. K. YIP, *Structure of stable solutions of a one-dimensional variational problem*, ESAIM Control Optim. Calc. Var., 12 (2006), pp. 721–751 (electronic).

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