
The crystallization conjecture

Seminar report

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Abstract

This seminar report deals with the open problem of crystallization in mathematics. It is based on the review article *The crystallization conjecture: a review* by Xavier Blanc and Mathieu Lewin [1]. Crystallization refers to the periodic arrangement of system particles as an energetically favourable equilibrium. From a mathematical point of view this refers to studying the minima of the system's energy. To lower the barrier to entry regarding the mathematical approaches, a few visual examples as well as chemical and physical theory concerning crystallization will be presented during the report. Next we will introduce the mathematical model. Lastly open problems will be elaborated upon and conjectures will be stated.

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1 Introduction



Figure 1: Crystals of rock sugar with flat faces reproduced from [2]

Crystals are used daily by humans everywhere around the globe in many different ways, examples being sugar (see Figure 1), table salt and even diamonds. Since crystals are in high demand, millions of tons are produced annually (see Table 1). Production approaches vary from single batches to continuous integrations. This is done to cater to the specific needs of customers such as particle size, purity or just sheer mass.

Product	Produced in	Production (t/a)
Sodium chloride	2001 in the EU	38.350.000
Sugar	2001 in the EU	15.000.000
Caprolactam	2002 worldwide	3.500.000
Ascorbic acid	2009 worldwide	110.000
Acetylsalicylic acid	2008 worldwide	35.000

Table 1: Annual production of commonly used crystals reproduced from [3]

It is therefore safe to state that crystals have an impact on day to day life. The millions of annually produced tons indicate that chemists and engineers involved in the production have fully understood the production of crystals. However the same can not be said regarding the mathematical modelling of crystal formation. This topic is still an open problem that needs more research.

This seminar report, based on the review article *The crystallization conjecture: a review* by Xavier Blanc and Mathieu Lewin [1], tries to shed light on this topic. A few chemical remarks regarding crystallization will be given in Section 2. Afterwards the mathematical model of crystal formation will be elaborated upon (see Section 3). Finally some current findings and open problems will be addressed in Section 4.

2 Crystallization

Crystals are homogeneous solids, whose particles are ordered in a periodic manner [4, p. 641]. The general study of the field of crystals is called crystallography. The specific term crystallization is the transition of single or multiple chemical substances from an amorphous, liquid or gaseous into a crystalline state [5, p. 105]. In the following sections some basic chemical concepts regarding the topic of crystals and their creation, will be given. The focus will be on three main topics regarding crystallization. These topics are supersaturation as the driving force behind crystallization, nucleation and how a crystal grows. Furthermore, in order to anticipate the subsequent mathematical discussion, different kinds of lattices and the Lennard-Jones potential will be discussed. Understanding lattices will be necessary for the modelling of crystal growth, while the Lennard-Jones potential will be extensively used in the later parts of this report to model the interactions between the crystal's particles.

2.1 Supersaturation

In order for the formation of a crystal to take place, several conditions have to be fulfilled. Similar to other chemical reactions, the environment temperature is of importance. Furthermore the ionic strength of atoms forming the crystal is essential. However the most important aspect is the supersaturation of the solution [5, pp. 112-113]. Consider for example a solvent and a dissolved substance (the solute). Under normal circumstances there is an equilibrium regarding how much solute can be dissolved in the solvent. If the concentration of the solute is artificially elevated beyond this equilibrium concentration the solution is supersaturated [5, p. 112]. The solution therefore is not in a state of thermodynamic equilibrium anymore. The setting for crystallization to occur is thus a solution where there is a surplus of solute that can then be used for crystal formation. Supersaturation for example can be achieved by evaporating a part of the solvent (evaporation crystallization) or by introducing additional substances that lower the solubility of the other solute in the solvent.

2.2 Nucleation

To re-establish equilibrium in the supersaturated solution, the process of so-called nucleation takes place. Nucleation relieves the supersaturation by creating crystals through self assembly of the dissolved particles [5, p. 113]. Nucleation thus lowers the concentration of the solute back to the equilibrium by creating crystals. There are two different forms of nucleation:

- Primary nucleation refers to the formation of crystals in the solution either with or without the addition of seed crystals [6, p. 15]. Seed crystals can either consist of the same chemical substances as the solute or something entirely different, even dirt particles in the solution. They can be introduced into the solution to promote the growth of crystals that could (depending on the desired product) otherwise take weeks or months to form. Therefore seed crystals accelerate crystallization since it is easier for crystals to form on an already existing surface [5, p. 113]. If there are no seed crystals present the nucleation is considered to be homogeneous, otherwise it is heterogeneous. However homogeneous nucleation is not very common since even the smallest impurities in the solution can be considered as seed crystals [7, p. 192].
- Secondary nucleation on the other hand refers to the fission of existing crystals which can also be related to the addition of seed crystals [6, p. 113]. Essentially existing crystals can break apart, thus creating more crystals in the solution and more surfaces for further crystal growth.

While secondary nucleation can occur under small amounts of supersaturation, primary nucleation requires a much higher level [7, p. 195]. Therefore primary nucleation is more difficult to achieve.

2.3 Lattices

Before we elaborate on crystal growth, we will first introduce the notion of lattices, since the most distinguishable property of crystals is their periodic structure. To explain the process of crystal growth we require basic understanding of the building blocks that compose such periodic structures. The smallest ordered assembly of particles in a periodic structure is called a unit cell [3, p. 9]. These repeating unit cells make up the entire crystal and define its structure. The most relevant lattices for crystals are called the Bravais lattices, which are defined as follows [8, p. 179].

Definition 1. Let $\{x_j\}_{j \in \mathbb{N}} \subseteq \mathbb{R}^3$ denote the positions of a collection of particles. We say that these particles form a Bravais lattice if there exist three basis vectors $\{v_i\}_{i=1,2,3} \subseteq \mathbb{R}^3$ such that $\forall j \in \mathbb{N}$ there exist integers n_{j1}, n_{j2}, n_{j3} with

$$x_j = n_{j1}v_1 + n_{j2}v_2 + n_{j3}v_3. \quad (1)$$

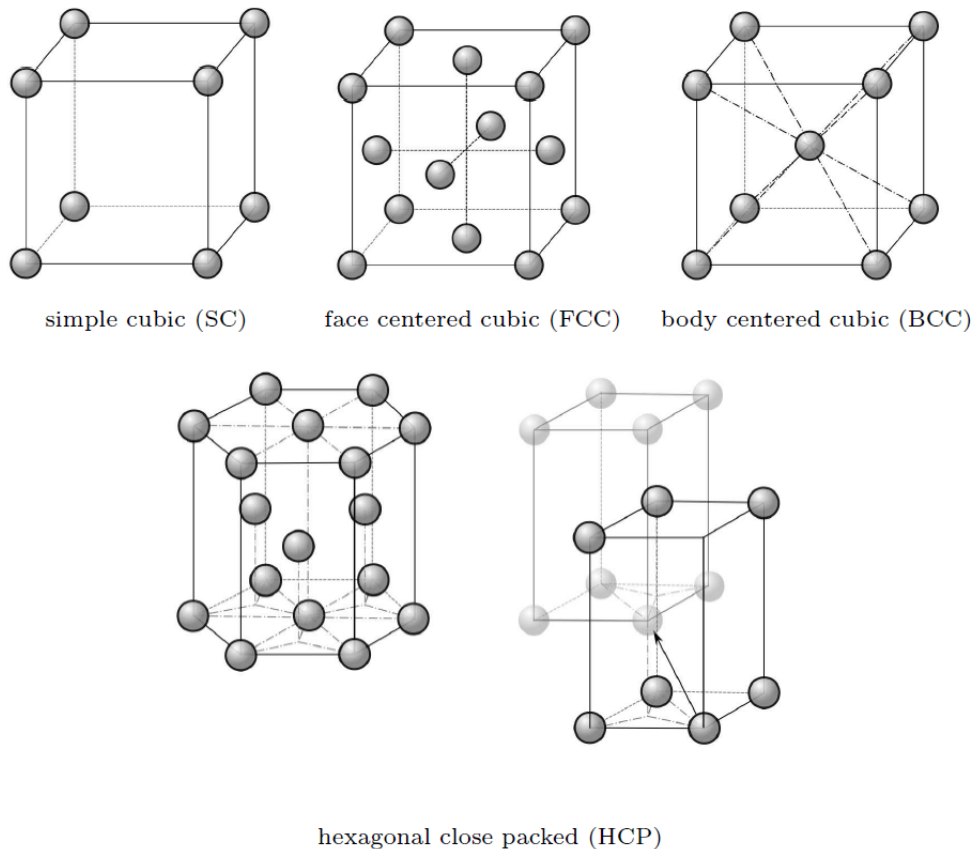


Figure 2: Common lattices in 3D reproduced from [1, p. 9]

In Figure 2, a few common examples of lattices are displayed. The simple, face centered and body centered cubic lattices are all part of the Bravais lattices [1, p. 8]. However the hexagonal close packed lattice (HCP) is not since it is a superposition of two shifted hexagonal Bravais lattices. The hexagonal Bravais lattice is similar to the HCP lattice but devoid of the three particles in the center of the unit cell. In the bottom right image of Figure 2 a neighbouring simple cubic lattice is displaced by about half the height of the cube in the vertical direction. By performing a similar translation for hexagonal lattices a HCP lattice can be created. A 2D example of two translated hexagonal lattices is shown in Figure 3 below.

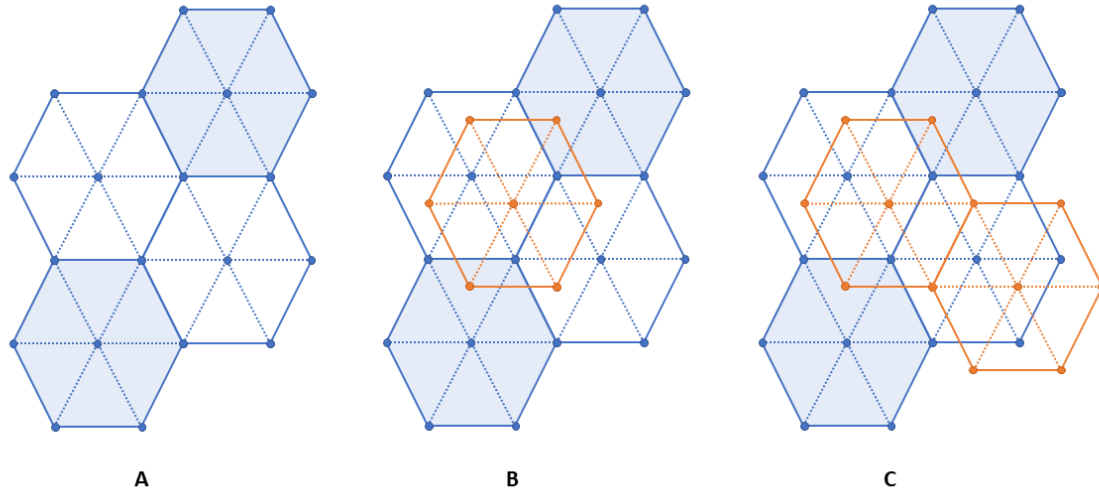


Figure 3: A: The lower parts of four hexagonal lattice unit cells, viewed from the top. B: A translated lower part of a second hexagonal lattice (depicted in orange), that is elevated in the viewing direction, was added. C: Addition of a second, translated unit cell in the "elevated layer".

In three dimensions it can be shown that there are a total of 14 different Bravais lattices [9]. Bravais lattices are the basis for all crystals that can be found in nature except quasicrystals, which have an ordered structure but do not consist of periodic unit cells. Bravais lattices are thus of major importance in crystallography.

2.4 Crystal growth

In Section 2.2, the formation of crystals was already linked to the process of nucleation, as a means of re-establishing a concentration equilibrium in the solution. The smallest agglomeration of particles that can grow to become a crystal is called a nucleus [7, p. 181]. From an informal point of view, the nucleus grows by agglomeration of other crystal building blocks or unit cells. However there is no technical difference between a nucleus and a bigger crystal apart from the difference in size.

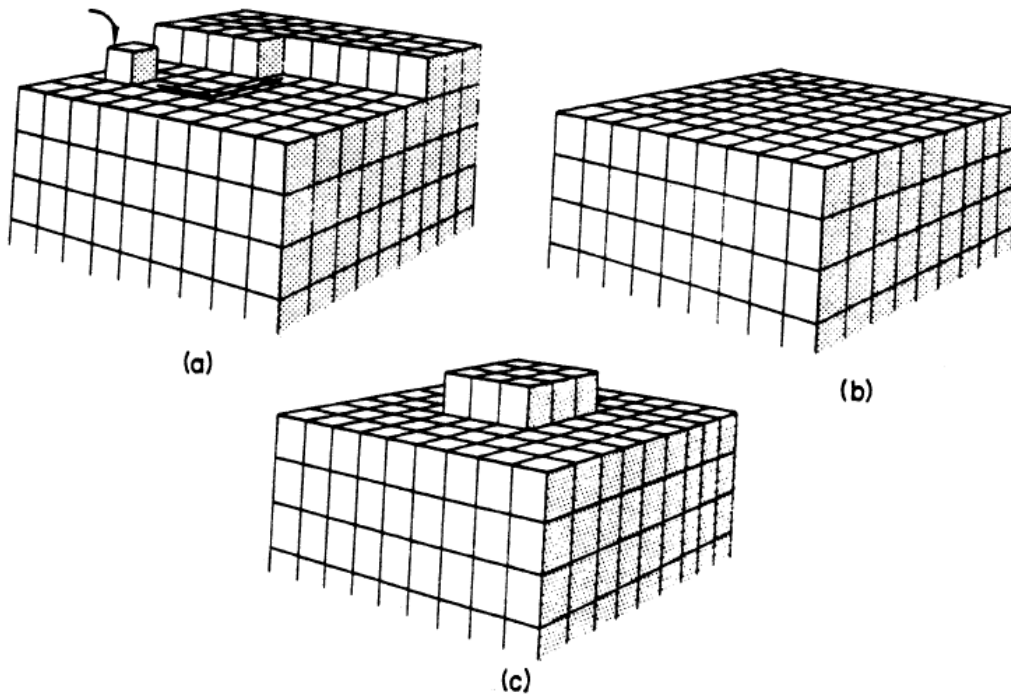


Figure 4: Ideal growth of a crystal's surface. (a) Surface diffusion towards an energetic favourable location, (b) Finished surface layer, (c) Newly formed nucleus on the surface reproduced from [7, p. 218]

A visually appealing way to explain the actual process of crystal growth is the Adsorption Layer theory, postulated by Volmer in 1939 and based on thermodynamics [7, p. 218]. This theory postulates that there are multiple steps in incorporating another building block into the crystal's surface [6, p. 20]. To explain the main idea of this theory, let us assume the most simple form of a cubic building block (simple cubic) as seen in Figure 2. A newly adsorbed building block will then search for an energetically favourable position on the existing crystal's surface and slot into this so called kink (see Figure 4 (a)). This process will proceed until the complete layer is finished (see Figure 4 (b)). Afterwards a new nucleus will build on the crystal's surface and the cycle will start again (see Figure 4 (c)).

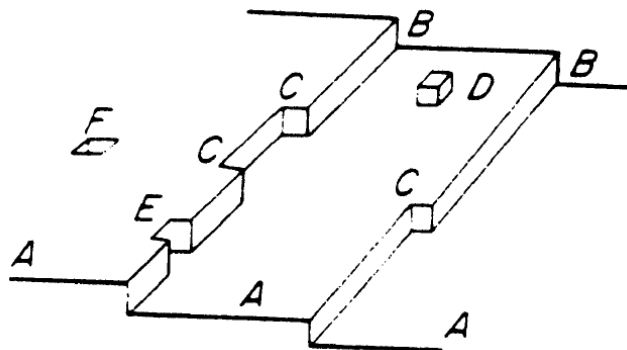


Figure 5: Kossel model of a crystal surface. (A) flat surfaces, (B) steps, (C) kinks, (D) surface absorbed building blocks, (E) vacancies on edges, (F) vacancies on surfaces reproduced from [7, p. 220]

An evolution of this concept is the Kossel model [7, p. 220] depicted in Figure 5. In the Kossel model multiple positions ((E) and (F)) exist that do not fully comply with the ideal growth assumption of the Adsorption Layer theory. This is based on the observation that real crystals do in fact contain tiny imperfections [7, p. 27]. Furthermore instead of a single layer of growth, there are multiple layers, each with the height of a single building block. The governing concept however remains the same. First, the building block diffuses towards the surface of the crystal where it is adsorbed (see Figure 5 (D)). Next the block seeks a kink towards which it diffuses. This process is called surface diffusion. When the block reaches this energetically favourable position, it settles in and is integrated into the crystal's structure. The crystal thus grows as adsorption and diffusion occur repeatedly. As in the Adsorption Layer model, new layers are created by surface nucleation.

Note that both of these models have the problem of not being able to accurately describe the rate of crystal growth for low levels of supersaturation in which surface nucleation does not occur frequently [7, p. 220].

Improvements to the Adsorption Layer theory were proposed by F.C. Frank in 1949 who postulated that a correct model for crystallization has to consider that most crystals contain dislocations [7, p. 220]. Screw dislocations create imperfections on the crystals surface allowing spiral structures to form, thus diminishing the need of surface nucleation (see Figure 6). Based on these improvements, cases with low levels of supersaturation can be modelled more accurately as well.

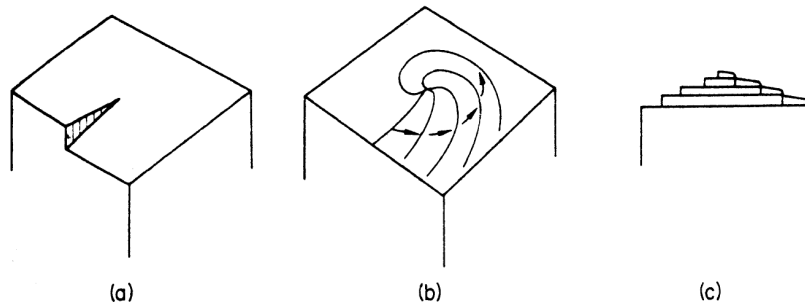


Figure 6: A developing spiral growth based on an imperfection can be seen in (a). The direction of the growth as seen from above can be seen in (b). The formed spiral can be seen from the side in (c). Reproduced from [7, p. 221]

Multiple other models regarding the growth of crystals such as the Surface Energy theory (which led to the foundation of the Adsorption theory) or the birth and spread model have been proposed [7, p. 231]. However the Adsorption Layer model provides an intuitive visualization.

2.5 Lennard-Jones potential

As discussed in Section 2.4, crystals are formed through the bonding of individual particles. Describing the interatomic interactions between these particles is therefore the next step in understanding the mathematical modelling of crystallization. To this end, we provide an explanation of the widely used interatomic Lennard-Jones potential. A discussion of other interatomic potentials such as the Stockmayer or the Buckingham potential is outside the scope of this report.

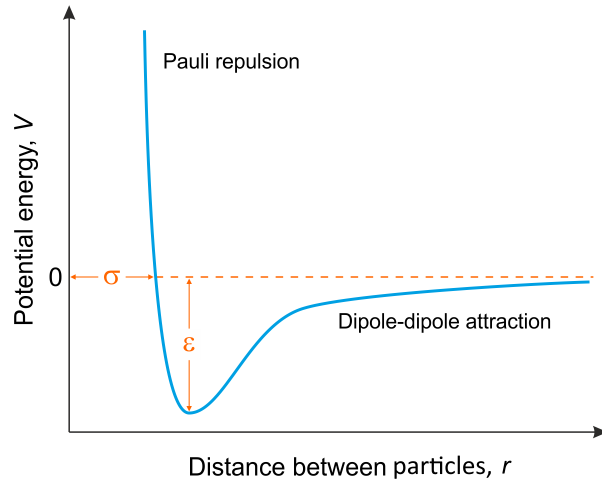


Figure 7: Lennard-Jones potential V plotted against the distance between two particles r , showcasing repulsion and attraction of two particles based on their distance to each other. Reproduced from [10]

In 1924 Sir John Edward Lennard-Jones proposed the Lennard-Jones potential V_{LJ} as an interatomic potential [11, pp. 463-477] that models the interaction between two neutral particles such as atoms or molecules [12, p. 764]. The Lennard-Jones potential is widely used in molecular dynamics simulations due to its lower cost of computation.

Definition 2. Let $r, r_m, \sigma \in \mathbb{R}_{\geq 0}$ and $\varepsilon \in \mathbb{R}$. The $12 - 6$ (or $6 - 12$) Lennard-Jones potential $V_{LJ}: \mathbb{R} \rightarrow \mathbb{R}$ is then given by

$$V_{LJ}(r) := 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] = \varepsilon \left[\left(\frac{r_m}{r} \right)^{12} - 2 \left(\frac{r_m}{r} \right)^6 \right]. \quad (2)$$

Here r is the distance both particles are separated from each other (from center to center), while r_m is defined as the distance where the potential of the particles reaches its minimum (see Figure 7). σ specifies the distance at which the potential between two particles reaches 0, while ε denotes the minimum of the potential [12, p. 764]. Both σ and ε are specific to different atoms.

The first term in the LJ potential (with the exponent of twelve) models the short range repulsion between two particles, while the second term (with the exponent of six) describes the long range attraction of particles. A positive LJ potential implies repulsive forces between two particles and a negative potential signals attracting forces [1, p. 4]. Intuitively this situation can be visualised by imagining the two particles as balls connected by an elastic spring. If the balls get pulled too far apart the string will try pull them back together to balance the strain on itself. If the balls however get pushed together they will repel each other. V_{LJ} tending towards infinity when the two particles get too close to each other is known as the Pauli repulsion [13], which states that if two fermions get too close they will repel each other [14, p. 776]. Fermions are elemental particles such as electrons [8, p. 63].

3 The mathematical model

In this section we describe the mathematical model underlying crystal formation. The content of this section is predominantly based on [1].

3.1 Energy

Consider a collection of $N \in \mathbb{N}$ identical particles in \mathbb{R}^d (usually $d \in \{1, 2, 3\}$). These particles interact pairwise with each other through a potential V . This potential could, for example, be the Lennard-Jones potential (see Section 2.5). Let $\{x_i\} \in \mathbb{R}^d$ and $\{p_i\} \in \mathbb{R}^d$, $i \in \{1, \dots, N\}$, denote the positions and momenta of each individual particle. Then the Hamiltonian of the system is given by

$$\mathcal{H}_N(x_1, \dots, x_N, p_1, \dots, p_N) = \sum_{i=1}^N \frac{|p_i|^2}{2m} + \sum_{1 \leq i < j \leq N} V(|x_i - x_j|). \quad (3)$$

Here m is the mass of each particle while $|\cdot|$ is the Euclidean norm in \mathbb{R}^d . Note that the Hamiltonian represents the total energy of the system and is therefore the sum of the potential and the kinetic energy [15, p. 21]. The equilibrium states of the system amount to the minima of \mathcal{H}_N . If the temperature $T = 0$ the Hamiltonian does not contain a kinetic energy term. Equation (3) then simplifies to the potential energy

$$\varepsilon_N(x_1, \dots, x_N) = \sum_{1 \leq i < j \leq N} V(|x_i - x_j|). \quad (4)$$

In this setting ($T = 0$), it is sufficient to consider the minimization problem (4), which only depends on the positions $\{x_i\}$ of the particles $i \in \{1, \dots, N\}$. The equilibrium state is therefore defined as

$$E(N) := \inf_{\{x_i\}} \{\varepsilon_N(x_i), x_i \in \mathbb{R}^d, i \in \{1, \dots, N\}\}. \quad (5)$$

It can be shown that ε_N is invariant under translations and rotations [1, p. 3]. Therefore the total energy of the system does not change if the system is rotated or translated by a fixed vector. We are interested in the behaviour of $E(N)$ if $N \rightarrow +\infty$, since the periodicity that is needed for the formation of a crystal lattice only seems to appear if a large number of particles is present.

3.2 Particle binding and the existence of a minimizer for $E(N)$

The key question to be answered is whether a minimizer for $E(N)$ (as defined in Section 3.1) does exist. Let us briefly consider this question from a chemistry point of view. We know that particles bind to each other to achieve an energetically favourable state by "sharing" their electrons [16, p. 96]. Furthermore we know from Section 2.4 that crystals form through particle binding. A system of bonded particles, such as a crystal, should therefore have an energetic minimum at equilibrium and at least one minimizer for $E(N)$ should thus exist as well. Before the existence of this minimizer can be further discussed, we will elaborate upon the properties of the problem, which are going to be used in the subsequent sections as well.

First note that in physical settings the interactions between particles are always somewhat attractive [1, p. 4]. Therefore we can assume $\min V < 0$. Furthermore $E(2) = \min V$ and thus $E(2) < 0$ holds as well.

The energy in the system is subadditive, thus the following inequality holds

$$E(N + P) \leq E(N) + E(P), \quad \forall N, P \geq 1. \quad (6)$$

We can prove Inequality (6) by translating P particles towards infinity and $V \rightarrow 0$ for a sufficiently large distance between particles. The translation leads to the disappearance of the

attraction between the two sets of particles and thus to overall weaker interactions between the sets and larger total energies. Mathematically we have

$$E(N + P) \leq \lim_{\substack{|\tau| \rightarrow \infty \\ \tau \in \mathbb{R}^d}} \varepsilon_{N+P}(x_1, \dots, x_N, y_1 + \tau, \dots, y_P + \tau) = \varepsilon_N(x_1, \dots, x_N) + \varepsilon_P(y_1, \dots, y_P). \quad (7)$$

Because this has to hold for all ε_N and ε_P , it will also hold for the respective infimums of $\varepsilon_N(x_1, \dots, x_N)$ and $\varepsilon_P(y_1, \dots, y_P)$ which leads to (6). Furthermore applying (6) inductively results in the following statement.

Lemma 1. $E(N) \leq \lfloor \frac{N}{2} \rfloor E(2) \leq (N - 1) \frac{E(2)}{2}$, for $N \in \mathbb{N}$, where $\lfloor \cdot \rfloor$ refers to the floor function.

Proof. The basic idea behind the proof of the first inequality is to successively translate 2 particles away from the system of $N \in \mathbb{N}$ particles so that the whole system is spread out. In accordance with the subadditivity of the system's energy $E(N)$ this results in

$$E(N) \leq E(N - 2) + E(2) \leq E(N - 2 \times 2) + 2E(2) \leq \dots \leq \frac{N}{2} E(2). \quad (8)$$

Applying the floor function then leads to the base form of the first inequality

$$E(N) \leq \left\lfloor \frac{N}{2} \right\rfloor E(2). \quad (9)$$

The second inequality can be proven as follows. We have

$$\left\lfloor \frac{N}{2} \right\rfloor = \begin{cases} \frac{N-1}{2} & \text{if } N \text{ is odd} \\ \frac{N}{2} & \text{if } N \text{ is even} \end{cases} \quad (10)$$

Thus

$$\left\lfloor \frac{N}{2} \right\rfloor \geq \frac{N-1}{2} \quad \forall N. \quad (11)$$

Since $E(2) < 0$, we have

$$\left\lfloor \frac{N}{2} \right\rfloor E(2) \leq \frac{N-1}{2} E(2). \quad (12)$$

Hence Lemma 1 holds. □

In view of Lemma 1, the optimal energy $E(N)$ is negative as well as constrained by an expression that is linear in the number of particles N .

Based on these two observations we obtain

$$\frac{E(N)}{N} \leq \frac{E(2)}{2} \left(1 - \frac{1}{N}\right) < 0. \quad (13)$$

After assessing the properties of the problem the question remains whether a minimizer exists. The Problem (5) possesses at least one minimizer if the *strict binding inequality*

$$E(N) < E(K) + E(N - K), \quad (14)$$

holds $\forall K \in \{1, \dots, N - 1\}$ and if V is continuous on $(0, \infty)$ [1, p. 5]. Notice that the only difference between inequalities (6) and (14) is, that in Inequality (14) we have strict inequality and in Inequality (6) we have non-strict inequality. If we start from Inequality (14) we can apply the same steps we took to obtain Inequality (13) and additionally obtain the existence of a minimizer, using the fact that $V < 0$ at infinity.

3.3 Stability

Based on the knowledge about the existence of a minimizer for $E(N)$ the next step is to evaluate whether the potential V is stable or not. We say that a potential V is stable if the potential energy per particle is bounded from below by a constant $C \in \mathbb{R}_{\geq 0}$ which is independent of the number of particles N (see Equation (16)) [17]. It is necessary for V to be stable since a stable potential is mandatory for the existence of an equilibrium.

For the existence of this constant C we require that the following limit exists and is finite

$$e_\infty = \lim_{N \rightarrow +\infty} \frac{E(N)}{N}. \quad (15)$$

The limit (15) can be understood as the average energy per particle if the system is at equilibrium and if the number of particles N is sufficiently large. This limit exists due to (13) and is based on the prior deduction from Section 3.2 that $\min V < 0$ as well as $V \rightarrow 0$ at infinity. As the next lemma shows, Equation (15) implies the existence of the constant $C \in \mathbb{R}_{\geq 0}$, independent of N such that $\forall N \in \mathbb{N}$

$$E(N) = \sum_{1 \leq i < j \leq N} V(|x_i - x_j|) \geq -CN. \quad (16)$$

Here $x_1, \dots, x_N \in \mathbb{R}^d$ are as introduced in Section 3.1.

Lemma 2. *For all $N \in \mathbb{N}$ it holds that*

$$e_\infty = \lim_{N \rightarrow +\infty} \frac{E(N)}{N} = \inf_{N \geq 1} \frac{E(N)}{N}. \quad (17)$$

Proof. Let I be defined as

$$I = \inf_{N \geq 1} \frac{E(N)}{N}. \quad (18)$$

Let L be any number greater than I and choose $M \in \mathbb{N}$ such that $L > \frac{E(M)}{M}$. Furthermore let $N = qM + r > M$, for some $0 \leq r < M$ and $q \in \mathbb{N}$. Similar to the previous Section 3.2 we assume subadditivity for E . Then the following statement holds

$$E(\underbrace{qM + r}_{=N}) = E(M + \dots + M + r) \leq \underbrace{E(M) + \dots + E(M)}_{q \text{ times}} + E(r) \leq qE(M) + E(r). \quad (19)$$

A division by N therefore leads to

$$\frac{E(N)}{N} \leq \frac{qE(M) + E(r)}{N} = \frac{qM}{N} \frac{E(M)}{M} + \frac{E(r)}{N}. \quad (20)$$

If $N \rightarrow +\infty$, $\frac{qM}{N} \rightarrow 1$ (since $N = qM + r$) and $\frac{E(r)}{N} \rightarrow 0$ (since $E(r)$ is bounded by the maximum of $E(i)$, for $0 \leq i < M$). We thus obtain

$$I = \inf_{N \geq 1} \frac{E(N)}{N} \leq \underbrace{\lim_{N \rightarrow +\infty} \frac{E(N)}{N}}_{=e_\infty} \leq \frac{E(M)}{M} < L. \quad (21)$$

We chose L as any number greater than I and therefore if $L \rightarrow I$ this leads to $\frac{E(M)}{M} \rightarrow I$ and $e_\infty \rightarrow I$ according to the above equation. Thus we finally obtain

$$I = \inf_{N \geq 1} \frac{E(N)}{N} = e_\infty = \lim_{N \rightarrow +\infty} \frac{E(N)}{N}. \quad (22)$$

□

Lemma 2 yields $C = -e_\infty$ as the best constant for (16), since e_∞ is also the minimal energy per particle. We thus restrict ourselves to only choose potentials V for which Equation (16) is satisfied. The system of particles will therefore be able to achieve an equilibrium configuration.

A simple example of a stable potential is:

$$V = V_1 + V_2, \text{ where } V_1 \geq 0, \hat{V}_2 \geq 0 \text{ with } \int_{\mathbb{R}^d} \hat{V}_2 < +\infty. \quad (23)$$

Here \hat{V}_2 denotes the Fourier transform of $x \rightarrow V_2(|x|)$. Unfortunately it is not possible to write several physical potentials in the proposed way of equation (23).

Another example of a stable potential is given through Proposition 1 [18, pp. 566-581].

Proposition 1. *Let $a, b \in \mathbb{R}$, while $0 \leq a \leq b < \infty$. Furthermore let $\varphi_1 : (0, a) \rightarrow \mathbb{R}$ and $\varphi_2 : (b, \infty) \rightarrow \mathbb{R}$ be two positive decreasing functions that satisfy the following conditions*

$$\int_0^a \varphi_1(r) r^{d-1} dr = \infty, \quad (24)$$

$$\int_b^\infty \varphi_2(r) r^{d-1} dr < \infty. \quad (25)$$

Let the potential $V : \mathbb{R}_{\geq 0} \rightarrow \mathbb{R}$ be given by

$$V(r) \geq \begin{cases} \varphi_1(r) & \text{for } 0 \leq r \leq a, \\ -C & \text{for } a \leq r \leq b, \\ -\varphi_2(r) & \text{for } r \geq b, \end{cases} \quad (26)$$

where $C \in \mathbb{R}$ is a constant. Then V is stable.

Consider Proposition 1. Notice that the rapid increase at 0 in Equation (24) avoids that particles can come too close towards each other. Intuitively this behaviour models the Pauli repulsion (see Section 2.5).

The conditions (24), (25) and (26) are met by the Lennard-Jones potential (for $d \leq 5$), which can therefore be regarded as stable in these dimensions.

3.4 Macroscopic objects

In the previous sections 3.2 and 3.3 we came to the conclusion that a minimizer for Problem (5) and an equilibrium for the particles in the system exist under certain conditions such as the strict binding inequality and the stability of the potential. However so far we do not know if the existence of a minimizer results in the formation of a macroscopic object.

Consider a system of $N \in \mathbb{N}$ particles for which the minimisation problem (5) has been solved. Therefore the positions of the system's particles $x_i, i \in \{1, \dots, N\}$ at equilibrium are known. Next, consider the following empirical measure

$$M_N = \frac{1}{N} \sum_{i=1}^N \delta_{\frac{x_i}{N^{1/d}}}. \quad (27)$$

Here $\delta_{\frac{x_i}{N^{1/d}}}$ represents a Dirac measure at each particle's position x_i and $N^{1/d}$ is a dilation factor. To evaluate the formation of a macroscopic object we consider a subsequence of measures

M_{N_j} defined by (27) and analyse whether it converges to some function $M \in L^\infty(\mathbb{R}^d)$ in the following sense

$$M_{N_j}(\cdot - \tau_j) \rightharpoonup M \text{ weakly-}^* \text{ in the sense of measure for some } M \in L^\infty(\mathbb{R}^d), \quad (28)$$

$$\text{supp}(M) \text{ compact and } \int_{\mathbb{R}^d} M(x) dx = 1.$$

Here M denotes the probability density function of a macroscopic object in \mathbb{R}^d . Therefore the support of M needs to be compact since any "real" object is "finite". We remind the reader that a sequence of measures μ_n is said to converge in a weak* sense to μ if

$$\lim_{n \rightarrow \infty} \int_{\mathbb{R}^d} f d\mu_n = \int_{\mathbb{R}^d} f d\mu, \quad (29)$$

holds for all continuous and bounded functions f .

Here the main idea is to take a subsequence of measures M_{N_j} , translate the system by a vector τ_j and then evaluate if the subsequence converges to the limit M in the sense of (28). If the system is continuous at the macroscopic scale with the function M being the local density then a macroscopic object has been formed. As of now finding the conditions for a potential V that result in the existence of the weak limit (28) has not been solved or even broadly studied [1, p. 7].

4 The crystallization conjecture

We will now discuss whether a system of N particles becomes periodic as $\lim N \rightarrow \infty$. Subsequently the results of other works regarding the mathematical modelling of crystal formation will be introduced.

4.1 Formulation

The main question regarding the mathematical modelling of crystal formation is whether a system of $N \in \mathbb{N}$ particles becomes periodic if $\lim N \rightarrow \infty$. First we define the lattice $G \subset \mathbb{R}^d$ as

$$G := \left\{ \sum_{j=1}^d n_j v_j, n_j \in \mathbb{Z} \right\}, \quad (30)$$

where $B = \{v_1, \dots, v_d\}$ is the basis in the vector space \mathbb{R}^d . Thus the lattice G is similar to the Bravais lattices introduced in Definition 1. Furthermore we say that the lattice G consists of the cells $g \in G$, which are generated by linear combinations of the basis vectors $\{v_j\}_{1 \leq j \leq d} \subseteq \mathbb{R}^d$ (see Figure 8 below).

To evaluate if crystallization has occurred we have to determine whether the particles arranged themselves periodically or not. In order to do that we require a periodic measure μ . We say that a measure is periodic if there exists a lattice G such that $\mu(\cdot + g) = \mu$ holds for all cells $g \in G$. Furthermore let μ_N be an empirical measure defined as

$$\mu_N := \sum_{i=1}^N \delta_{x_i} \in \mathbb{R}, \quad (31)$$

based on the equilibrium positions of the system's particles x_i for $i \in \{1, \dots, N\}$ (and thus based on the solution of problem (5)). In contrast to Section 3.4 the observation remains at the microscopic level. However the stated idea of periodicity remains similar to (28). Consider a

subsequence of measures μ_{N_j} and a translation vector $\tau_j \in \mathbb{R}^d$. We say that crystallization has occurred, if the following statement holds for a periodic measure μ

$$\mu_{N_j}(\cdot - \tau_j) \rightarrow \mu. \quad (32)$$

An example of a more abstract but possible lattice is shown in Figure 8.

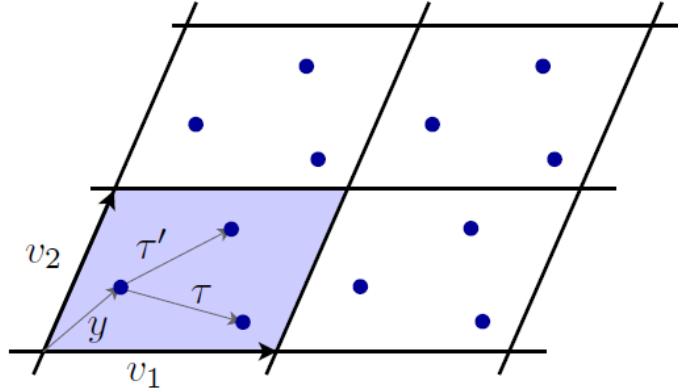


Figure 8: A possible 2D periodic lattice reproduced from [1, p. 8]

The configuration in Figure 8 is actually a superposition of three shifted crystalline lattices. In this case μ would thus be

$$\mu = \sum_{g \in G} \delta_{g+y} + \sum_{g \in G} \delta_{g+y+\tau} + \sum_{g \in G} \delta_{g+y+\tau'}, \quad (33)$$

where y , τ and τ' are fixed vectors in \mathbb{R}^d .

If the particles lie exactly on the vertices of the lattice G this is regarded as a Bravais lattice (see Section 2.3). An example for a 2D Bravais lattice would be a lattice with four particles per unit cell, where each particle lies on one of the cell's four corners. This lattice is similar to the simple cubic lattice in 3D (for reference see Figure 2). In this case μ would thus be

$$\mu = \sum_{g \in G} \delta_{g+y}, \quad (34)$$

where $y \in \mathbb{R}^d$ is a fixed vector that defines the position of the lattice.

Let us remark a priori that there is no correlation between the macroscopic and microscopic measures M_N and μ_N [1, p. 9]. Nonetheless the two should be connected to each other.

Lastly if crystallization can be proven based on the periodicity of the lattice G , then the next question is which form does the lattice have. Specifically does μ correspond to a Bravais lattice?

4.2 Crystallization results for $d = 1$

The crystallization problem has been understood comparatively well in one dimension. Venterogel and Nijboer proved that the limit e_∞ (see Section 3.3) is reached by equidistant configurations [19, pp. 343-361],[20, pp. 274-288],[21, pp. 569-580]. This was proven for multiple potentials including the Lennard-Jones potential. All considered potentials were repelling for close particles and attracting for particles far away from each other.

The convergence of (32) is still an open problem that has not been proven in a general case yet [1, p. 10]. For the special case of the Lennard-Jones potential, Gardner and Radin provided a proof in 1978 [22, pp. 719-724]. Furthermore there are some examples for which the resulting lattices do not correspond to Bravais lattices [19, pp. 355-356]. One example for this is the following potential $V : \mathbb{R} \rightarrow \mathbb{R}$ defined as

$$V(r) = \begin{cases} +\infty & \text{for } r < \frac{4}{9}, \\ 2 - 3r & \text{for } \frac{4}{9} \leq r \leq 1, \\ -(r^{-2}) & \text{for } r \geq 1. \end{cases} \quad (35)$$

Furthermore at equilibrium non-periodicity of the system's particles was achieved by introducing an oscillating potential [23, pp. 601-607]. Additionally non-periodicity has been proven for an arbitrary small perturbed potential for which crystallization would otherwise occur.

Thus it is safe to state that even in a single dimension the conditions that govern crystallization have not been fully understood yet. Furthermore there does not exist a single, unified result that proves the existence of crystallization solely under the assumptions of a stable, smooth, non-increasing (for $r < r_m$) and non-decreasing (for $r > r_m$) potential V [1, p. 10].

4.3 Crystallization conjectures for $d > 1$

In multiple dimensions the crystallization problem is far from being understood [1, p. 10]. The majority of the existing results for crystallization is based on a reduction to the sphere packing problem, since we already know the solutions to this problem. However the relation between the two problems requires further restrictions on the potential V , which we will address after a brief introduction to the sphere packing problem.

The sphere packing problem can be traced to Sir Walter Raleigh who was interested in determining the most efficient way to stack cannonballs [24, p. 1]. Hence the problem refers to the more general question of the densest packing of equally sized spheres that are not allowed to overlap. Incidentally Carl Friedrich Gauss proved that the highest percentage equally sized spheres can occupy in a given volume is about 74.05% [24, pp. 114-115].

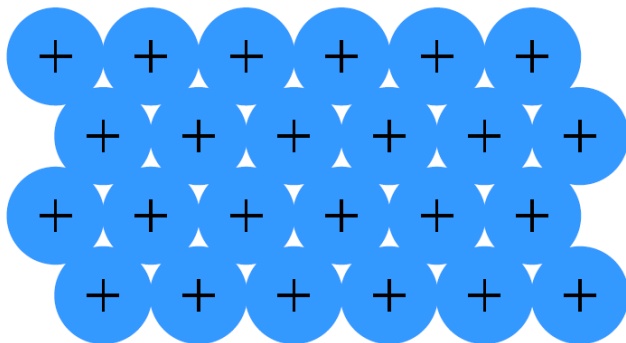


Figure 9: 2D packing of identical disks reproduced from [1, p. 11]

For two dimensions Tóth proved in 1940 that the optimal solution for the problem is a hexagonal lattice formed of the disk centers (see Figure 9) [25]. We will now outline a simple sketch of the proof [24, pp. 60-65]. Originally Tóth was interested in the maximum number of trees that could be put next to each other in an area A for a given separation D between the trees. He assumed that every tree needs a certain amount of space to properly grow, denoted by a disk of radius R around each tree. If the distance D is exactly two times the radius R ,

this is precisely the disk packing problem. Tóth was then drawn to the related problem of how to completely fill the area with the least amount of trees when the circles or disks could now overlap, while still keeping a distance D to each other. Finally he studied how to maximize the overlapping area of these circles.



Figure 10: Multiple neighbouring circles placed around a central circle C . Reproduced from [24, p. 63]

Tóth's idea was to begin with one central disk C and successively place further disks around the central one (see Figure 10). In theory the overlapping area should increase with the number of neighbouring disks around C . However this is only true for up to six neighbours. If we introduce seven instead of six neighbours, all of the outside disks will be pushed further away from C , because all disks still have to maintain the minimal distance D from each other. Therefore six neighbours, ordered in a hexagonal pattern, will result in the largest overlapping area or the smallest non-overlapping area for C .

It now remains to quantify the non-overlapping area of C . The overlapping areas basically belong to all the disks that overlap at a given position. Therefore Tóth simply divided each overlapping area by the number of disks that intersected at this position and attributed the area evenly to the overlapping disks. A simple example of this is the arrangement of the two overlapping disks in Figure 10. In this case we would divide the overlapping area by two and attribute each half to one disk each. For the configuration with six neighbouring disks the resulting area of the inner circle C is thus roughly $0.866D^2$, which is therefore the lower bound for the area of each tree. To answer Tóth's second question, he would thus need at least $\frac{A}{0.866D^2}$ trees to cover the area A if the trees' disks are allowed to overlap. With this lower bound we know that no packing of disks can be denser than the hexagonal one, which also applies to our relevant case of $D = 2R$.

Kepler posed the sphere packing problem (also known as Kepler's conjecture) as early as 1611 [24, p. 5], long before Tóth even began to study the subject. However it is exceedingly more complicated compared to only two dimensions. This is due to the existence of multiple solutions to the problem including the face centered cubic lattice, hexagonal close packed lattice (see Figure 2 for both) and non-periodic compositions as well.

The relation between crystallization and the sphere packing problem is done by geometrical arguments on the particles and is based on the assumption that particles, like atoms, can be modelled as spheres. Heitmann and Radin elaborated upon this relation between the two problems in [26, pp. 281-287]. For the following potential V , the particles of the system can be regarded as solid spheres with a radius of $\frac{1}{2}$:

$$V(r) = \begin{cases} +\infty & \text{for } 0 \leq r < 1, \\ -1 & \text{for } r = 1, \\ 0 & \text{for } r > 1. \end{cases} \quad (36)$$

Due to the condition $V(1) = -1$ the single particles are inclined to make contact with each other. Hence it is a suitable representation of the sphere packing problem. However a non-smooth potential V (such as the one above) does not fully represent the behaviour between particles. Additionally the assumption that particles (respectively spheres) can directly touch each other is not completely realistic due to Pauli repulsion (see Section 2.5). Furthermore the sphere packing problem is only capable of modelling mono-atomic crystals, due to the constraint that all spheres have to be of the same size. Therefore common crystals such as table salt or sugar can not be related to the sphere packing problem.

A proof for a more realistic potential (like the Lennard-Jones potential) without additional constraints has yet to be given [1, p. 11]. To conclude, even in 2D there is no complete understanding of the crystallization problem, since a lot of the results are based on the solutions to the sphere packing problem.

4.4 Fixed density

A slightly different approach is based on forcing the particles to stay together, thus rendering the need for constrained potentials V that guarantee the formation of a macroscopic object unnecessary. The principle behind this approach is minimizing the energy of the system while keeping the density ρ of the particles constant. To achieve this the particles are restricted to a domain Ω . Furthermore the number of particles N is related to the domain in the following manner

$$N \approx \rho |\Omega|. \quad (37)$$

Here $|\Omega|$ refers to the volume of Ω , while $\rho > 0$ is a fixed value in $\mathbb{R}_{\geq 0}$. In accordance with (37) we get a family of problems dependant on ρ , due to different combinations of N and $|\Omega|$. This results in a similar formulation to Problem (5)

$$E_{\Omega}(N) = \inf_{\{x_i\}} \{\varepsilon_N(x_i), x_i \in \Omega, i \in \{1, \dots, N\}\}. \quad (38)$$

Contrary to Equation (15), only increasing N would change the problem, since the particle density ρ would increase as well if $|\Omega|$ stays fixed. We therefore need to increase both N and $|\Omega|$ such that ρ stays constant. We thus introduce $\{\Omega_N\}_{N \in \mathbb{N}}$ as a sequence of domains that cover the whole space if $N \rightarrow \infty$.

Similar to the limit (15), a stable potential requires the existence of the following finite limit

$$e(\rho) := \lim_{\substack{N \rightarrow \infty \\ |\Omega_N| \rightarrow \infty \\ N/|\Omega_N| \rightarrow \rho}} \frac{E_{\Omega_N}(N)}{N}. \quad (39)$$

Compared to the limit (15), proving the existence of the limit in (39) tends to be more difficult, as we will shortly discuss.

Notice first that we can obtain two additional inequalities, based on the prior considerations in Section 3.2:

$$E_{\Omega}(N) \geq E(N) \geq e_{\infty} N, \quad e(\rho) \geq e_{\infty}, \quad \forall \rho > 0. \quad (40)$$

In the above inequalities $E(N)$ and e_{∞} are as defined in (5) and (15) respectively. However this still does not give us an upper bound for $e(\rho)$. This is because the introduction of the domain Ω does not allow us to send particles to infinity and therefore most properties we used

in Section 3.2 do not hold anymore. Additionally the energy is not necessarily subadditive like in Inequality (6). Thus $E(N) > 0$ may hold. Before (for an unbounded domain) we deduced that $E(N) < 0$ was true due to the fact that the particles could spread out from each other. However this is not true for a bounded Ω , where particles could be forced to stay close to each other, even if they would otherwise repel each other at such a close distance. Lastly V can not tend to zero too slowly or there could be an interaction between too many neighbouring particles which can lead to the energy growing faster than N . Consequentially the limit $e(\rho)$ from (39) may not exist and the potential would not be stable.

One way to solve these problems is to assume that V is integrable at infinity, which allows us to find a configuration of the system's particles that satisfies $E(N) \leq CN$ [1, p. 12]. For $E(N) \leq CN$ (with the stability condition (16)) it can be shown that the limit (39) exists and is independent of Ω_N . Under the above assumptions the goal remains similar to the prior sections, which is to analyse the behaviour of the system's particles and their positions $\{x_i\}$ as solutions to the problem (38). Ventevogel and Nijboer published results for the 1D case in 1978 [19, pp. 343-361]. They proved crystallization for any given density $\rho > 0$, if the potential is non-negative and non-increasing convex. But just as before, the solution for $d > 1$ is still an open problem and thus requires more research [1, p. 13].

4.5 The Jellium model

The potentials mentioned so far in this report concerned neutral particles such as atoms. However more realistic potentials (that can depict real interactions between charged particles) such as the Coulomb potential V_{Coul} have been studied as well [27, pp. 1002-1011]. The discrete Coulomb potential $V_{d,\text{Coul}} : \mathbb{R}^d \rightarrow \mathbb{R}$ is defined as

$$V_{d,\text{Coul}}(r) = \frac{1}{4\pi\epsilon_0} \sum_i \frac{q_i}{|r - r_i|}. \quad (41)$$

Here ϵ_0 is the permittivity of vacuum, q_i is the point charge at position $r_i \in \mathbb{R}^d$, for $i \in \{1, \dots, N\}$, where $N \in \mathbb{N}$ denotes the number of point charges. The main problem preventing crystallization of charged particles is that particles of the same charge will repel each other and thus the particles would try to maximize the distance between each other.

The solution to the crystallization problem for charged particles is to use external potentials. An external potential can allow for an equilibrium to form by balancing out the negative charge of the system of electrons. In practical experiments, we use two electrodes which are placed in a vacuum [28, p. 804], and used to create an alternating electric field. This installation is also referred to as ion trap since ions are kept from neutralizing their charge. Then a gas (for example methane) is introduced into the vacuum. Due to the potential between the two electrodes a weakly ionized plasma is created.

"Free" electrons can exist in the experiment because of the alternating, oscillating electrical field that keeps them from recreating neutral states. Next, a small amount of ionizable particles (for example carbon), is introduced into the ion trap, thus ionizing the particles, which now arrange in a lattice. Due to the electrical field the crystal lattice is furthermore somewhat stable and does not collapse as soon as the system's energy changes slightly.

Wigner considered a so called Jellium model, where electrons crystallise and arrange in a lattice to minimize their energy [27, pp. 1002-1011]. Jellium refers to a gas of uniform electrons. In this model the movement of the particles gets slowed down by a background referred to as "jelly". Even if it seems like a vast simplification of the problem it is possible for trapped systems to locally behave like Jellium [1, p. 17]. Thus making the approach physical relevant.

The Wigner minimization problem is given by

$$E_{\Omega,\rho}(N) := \inf_{\{x_i\}} \left\{ \sum_{1 \leq i < j \leq N} V(|x_i - x_j|) - \rho \sum_{i=1}^N \int_{\Omega} V(|x_i - y|) dy + \frac{\rho^2}{2} \int_{\Omega} \int_{\Omega} V(|x - y|) dx dy \right\}. \quad (42)$$

Here the first term accounts for the potential energy of the $N \in \mathbb{N}$ particles, while the second term models the interactions between the homogeneous background and the particles of the system [1, p. 18]. The third term describes the energy of the background, which is used to obtain the limit (43). Lastly ρ is the density of the particles in the domain Ω as introduced in Section 4.4.

As before we require that the potential is stable for the existence of an equilibrium. We thus require the existence of the following limit similar to (39):

$$e_{\text{Jell}}(\rho) := \lim_{\substack{N \rightarrow \infty \\ |\Omega_N| \rightarrow \infty \\ N/|\Omega_N| \rightarrow \rho}} \frac{E_{\Omega_N,\rho}(N)}{N}. \quad (43)$$

For 1D Kunz proved crystallization for charged particles in 1974 [29, pp. 303-335] but only for small densities. Aizenmann and Martin were later able to generalize this proof for any density [30, pp. 99-116].

Wigner conjectured crystallization for the continuous Coulomb potential V_{Coul} , if the density ρ is small enough and $1 \leq d \leq 3$ [27, pp. 1002-1011]. He also conjectured that the particles form a body centered cubic lattice in 3D. In 2D however, he suspected that the particles form a hexagonal lattice. While Wigner's conjectures for the lattice configurations in two and three dimensions are supported by numerical simulations, mathematical proofs for $d > 1$ are still missing.

5 Conclusion

Several million tons of crystals are produced annually. And while these processes function well, there exist underlying mathematical questions which have not yet been answered. While there are some results and solutions for crystallization in one dimension, for example in case of the Lennard-Jones potential (see Section 4.2), the understanding of the cases for $d > 1$ is much less clear. Typically the existing solutions require additional constraints such as fixed densities or temperatures. Even though the first questions on this subject have been around for hundreds of years (dating back to Kepler), further research still needs to be done. Although the mathematical background is far from being easy to understand, the chemical approach in this report and the addition of small proofs hopefully made the topic easier to understand.

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