



Effect of Periodic Arrays of Defects on Lattice Energy Minimizers

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Abstract. We consider interaction energies $E_f[L]$ between a point $O \in \mathbb{R}^d$, $d \geq 2$, and a lattice L containing O , where the interaction potential f is assumed to be radially symmetric and decaying sufficiently fast at infinity. We investigate the conservation of optimality results for E_f when integer sublattices kL are removed (periodic arrays of vacancies) or substituted (periodic arrays of substitutional defects). We consider separately the non-shifted ($O \in kL$) and shifted ($O \notin kL$) cases and we derive several general conditions ensuring the (non-)optimality of a universal optimizer among lattices for the new energy including defects. Furthermore, in the case of inverse power laws and Lennard-Jones-type potentials, we give necessary and sufficient conditions on non-shifted periodic vacancies or substitutional defects for the conservation of minimality results at fixed density. Different examples of applications are presented, including optimality results for the Kagome lattice and energy comparisons of certain ionic-like structures.

Mathematics Subject Classification. Primary 74G65; Secondary 82B20.

Keywords. Lattice energy, Universal optimality, Defects, Theta functions, Epstein zeta functions, Ionic crystals, Kagome lattice.

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1. Introduction, Setting and Goal of the Paper

1.1. Lattice Energy Minimization, Summary of Our Results and Setting

Mathematical results for identifying the lattice ground states of interacting systems have recently attracted a lot of attention. This problem is also called ‘Crystal Problem’ in [43] and asks whether the following ‘Crystallization Conjecture’ [16] is true: For relevant interactions, ground states, seen as energy minimizers, of interacting particles systems at low temperature are always periodic. This is mainly motivated by the periodic solid state of matter and the rich spectrum of structures existing in nature, from the Polonium’s simple cubic one only built from one type of atoms to the Sodalite composed by four different species. It is also well known that matter can have complicated almost periodic structures as quasicrystals. Therefore, one can ask how the shape of the interaction potentials yields both to periodic (or almost periodic) minimizers and to certain types of lattice ground states. Looking at the number of parameters involved in this problem, it is obviously a very difficult mathematical question.

Even though the Crystal Problem is still open in full generality, many interesting results have been derived in various settings for showing the global minimality of certain periodic structures including the uniform chain \mathbb{Z} , the triangular lattice A_2 , the square lattice \mathbb{Z}^2 , the face-centered cubic lattice D_3 (see Fig. 1), as well as the other best packings E_8 and the Leech lattice Λ_{24} (see [12, 24] and references therein). Moreover, the same kind of investigation has been made for multi-component systems (e.g., in [10, 30, 31, 36, 37]) where the presence of charged particles yield to rich energetically optimal structures. These problems of optimal point configurations are known to be at the interface of mathematical physics, chemistry, cryptography, geometry, signal processing, approximation, arithmetic, etc. The point of view adopted in this work is the one of material science where the points are thought as particles or atoms.

In this paper, our general goal is to show mathematically how the presence of periodic arrays of charges (called here ‘defects’ in contrast to the initial crystal ‘atoms’) in a perfect crystal affects the minimizers of interaction energies when the interaction between species is radially symmetric. Since the structure of crystals is often given by the same kind of lattices, it is an important question to know the conditions on the added periodic distribution of defects and on the interaction energy in order to have conservation of the

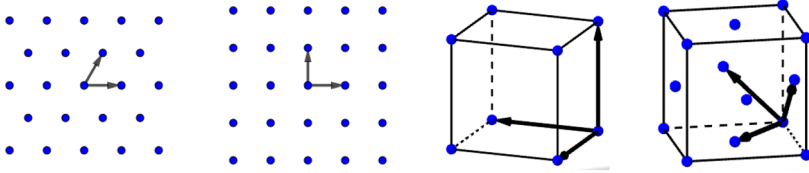


FIGURE 1. In dimension $d = 2$, representation of the triangular and square lattices, respectively, defined by $A_2 = \lambda_1 [\mathbb{Z}(1, 0) \oplus \mathbb{Z}(1/2, \sqrt{3}/2)]$ and \mathbb{Z}^2 . In dimension $d = 3$, representation of the simple cubic and the face-centered cubic lattices, respectively, defined by \mathbb{Z}^3 and $D_3 := \lambda_2 [\mathbb{Z}(1, 0, 1) \oplus \mathbb{Z}(0, 1, 1) \oplus \mathbb{Z}(1, 1, 0)]$. The constants λ_1, λ_2 are such that the lattices have unit density

initial ground state structure. Only very few rigorous results are available on minimization of charged structures among lattices. Our motivation takes its source in our recent works [9, 10] where the rock-salt structure (i.e., the simple cubic lattice with an alternation of charges ± 1) has been shown to be the good candidate for the Crystal Problem with different types of charges, whereas the usual optimizers are $A_2, D_3, E_8, \Lambda_{24}$ as explained above. Therefore, investigating the effects of charges in such crystal systems appears to be very interesting.

More precisely, we are considering building blocks of the total interaction energy of a multi-component lattice crystal, i.e., the interaction energy between one particle placed at the origin of \mathbb{R}^d and the others species located on the sites of a simple lattice (see Sect. 1.2). This choice is motivated by the high difficulty to minimize sums of lattice energies with competing behaviors (see, for instance, Remark 2.7 as well as [10]), since the total energy per point of the system is in general the averaged sum of different lattice energies (see Sect. 1.2). The ‘trick’ to get different species on lattices is to remove a certain number of times certain sublattices from the original one. The ‘charges’ or ‘weights’ located on these sublattices sites change altogether and yield to a new ionic crystal structure, possibly with vacancies (see, e.g., Figs. 2 and 3). We then ask the following question: Does the minimizer among lattices of the interaction energy between the origin and the new charged lattice change with respect to the identical particle case (i.e., without changing any sublattice)? One can ask this question for any type of periodic or almost periodic structure, but the aim of this paper is to investigate this problem for simple lattice structures for which many minimality results are available (see below).

We now give a very short description of our results. In the Gaussian case, if the charges decrease on the chosen sublattices, then the minimizer changes with respect to the Gaussian parameter, whereas it is conserved when the charges increase (see Theorem 2.2). We therefore derive conditions on charges and sublattices such that optimality results are conserved (see Theorems 2.4 and 2.9 as well as Corollary 2.13) or not (see Theorem 2.11) after the addition

of infinite periodic arrays of defects. In particular, inverse power laws and Lennard-Jones-type potentials are studied (see Theorems 2.15 and 2.17). These results are pushing a step forward the understanding of ground states for interaction energies with radially symmetric potentials. Furthermore, our main concrete applications include new optimality properties for the Kagome lattice and other ionic compounds with charges ± 1 as the rock-salt structure. The reader looking for such concrete examples is invited to read Sect. 3.

Let us now describe our setting more precisely. We assume the periodicity of our systems, and once we restrict this kind of problem to the class of (simple) lattices and radially symmetric interaction potentials, an interesting non-trivial problem is to find the minimizers of a given energy per point among these simple periodic sets of points, with or without a fixed density. In this paper, we keep the same kind of notations we have used in our previous works (see, e.g., [8, 10, 14]). More precisely, for any $d \geq 2$ we called \mathcal{L}_d the class of d -dimensional lattices, i.e., discrete co-compact subgroups of \mathbb{R}^d ,

$$\mathcal{L}_d := \left\{ L = \bigoplus_{i=1}^d \mathbb{Z}u_i : \{u_1, \dots, u_d\} \text{ is a basis of } \mathbb{R}^d \right\},$$

and, for any $V > 0$, $\mathcal{L}_d(V) \subset \mathcal{L}_d$ denotes the set of lattices with volume $|\det(u_1, \dots, u_d)| = V$, i.e., such that its unit cell Q_L defined by

$$Q_L := \left\{ x = \sum_{i=1}^d \lambda_i u_i : \forall i \in \{1, \dots, d\}, \lambda_i \in [0, 1] \right\}, \tag{1.1}$$

has volume $|Q_L| = V$. We will also say that $L \in \mathcal{L}_d(V)$ has density V^{-1} . The class \mathcal{F}_d of radially symmetric functions we consider is, calling \mathcal{M}_d the space of signed Radon measures on \mathbb{R}_+ ,

$$\begin{aligned} \mathcal{F}_d := \left\{ f : \mathbb{R}_+ \rightarrow \mathbb{R} : f(r) = \int_0^\infty e^{-rt} d\mu_f(t), \mu_f \in \mathcal{M}_d, |f(r)| \right. \\ \left. = O(r^{-p_f}) \text{ as } r \rightarrow \infty, p_f > d/2 \right\}. \end{aligned}$$

When μ_f is non-negative, f is a completely monotone function, which is equivalent by Hausdorff–Bernstein–Widder Theorem [3] with the property that for all $r > 0$ and all $k \in \mathbb{N}$, $(-1)^k f^{(k)}(r) \geq 0$. We will write this class of completely monotone functions as

$$\mathcal{F}_d^{cm} := \{f \in \mathcal{F}_d : \mu_f \geq 0\}.$$

As explained by Schoenberg in [47], it has been shown, using Bochner’s Theorem [17], that $f \in \mathcal{F}_d^{cm}$ if and only if $r \mapsto f(r^2)$ is the Fourier transform of a non-negative finite Borel measure on \mathbb{R} . Therefore, since we are going to sum these potentials f on the square of the lattice distances, this particular class of functions \mathcal{F}_d^{cm} is related to the one used by Ruelle [45, Prop. 1.2] in the context of superstable interaction potentials (i.e., potentials Φ where $\Phi \in \mathcal{F}_d^{cm}$). Furthermore, the same kind of interactions with non-negative Fourier transform

have been used by Sütő in [48, 49] in the context of high-density crystallization, but where their Fourier transform is zero outside a ball, leading to highly oscillating potentials.

In particular, the class \mathcal{F}_d^{cm} includes any inverse power law $f(r) = r^{-s}$ where $s > d/2$ corresponding to a repulsive interaction between positive charges (with Coulomb systems in mind). Moreover, the class \mathcal{F}_d is meant to be linear combinations of functions belonging to \mathcal{F}_d^{cm} including in particular Lennard-Jones-type potentials $f(r) = c_2 r^{-x_2} - c_1 r^{-x_1}$ where $(c_1, c_2) \in (0, \infty)$ and $x_2 > x_1 > d/2$.

For any $f \in \mathcal{F}_d$, we thus defined the f -energy $E_f[L]$ of a lattice L , which is actually the interaction energy between the origin O of \mathbb{R}^d and all the other points of L , by

$$E_f[L] := \sum_{p \in L \setminus \{0\}} f(|p|^2). \quad (1.2)$$

Notice that this sum is absolutely convergent as a simple consequence of the definition of \mathcal{F}_d . We could also define E_f without such decay assumption by renormalizing the sum using, for instance, a uniform background of opposite charges (see, e.g., [35]) or an analytic continuation in case of parametrized potential such as r^{-s} (see [18]). The fact that the origin is excluded from the above sum is motivated by two reasons: 0 is a fixed point of L when L varies in \mathcal{L}_d and f is not necessarily defined for $r = 0$ (e.g., when f is an inverse power laws or a Lennard-Jones-type potentials). We also notice that the linearity of $f \mapsto E_f[L]$ on \mathcal{F}_d will be widely used for writing energies in terms of completely monotone potentials, as well as a mathematical ‘trick’ for identifying defect and no-defect cases.

One can interpret the problem of minimizing E_f in \mathcal{L}_d (or in $\mathcal{L}_d(V)$ for fixed $V > 0$) as a geometry optimization problem for solid crystals where the potential energy landscape of a system with an infinite number of particles is studied in the restricted class of lattice structures. Even though the interactions in a solid crystal are very complex (quantum effects, angle-dependent energies, etc.), it is known that the Born–Oppenheimer adiabatic approximation used to describe the interaction between atoms or ions in a solid by a sum of pairwise contributions (see, e.g., [41, p. 33 and p. 945] and [52]) is a good model for ‘classical crystals’ (compared to ‘quantum crystals’ [19]), i.e., where the atoms are sufficiently heavy. Moreover, since all the optimality properties we are deriving in this paper are invariant under rotations, all the results will be tacitly considered up to rotations.

Furthermore, studying such interacting systems with this periodicity constraint is a good method to keep or exclude possible candidates for a crystallization problem (i.e., with free particles). We are in particular interested in a type of lattice L_d that is the unique minimizer of E_f in $\mathcal{L}_d(V)$ for any fixed $V > 0$ and any completely monotone potential $f \in \mathcal{F}_d^{cm}$. Following Cohn and Kumar [22] notion (originally defined among all periodic configurations), we call this property the *universal optimality among lattices* of L_d (or *universal optimality in $\mathcal{L}_d(1)$*), see Definition 2.1.

In this paper, we also study f -energies of shifted versions of lattices L , i.e., energies of type

$$L \mapsto E_f[L + x] := \sum_{\substack{p \in L \\ p+x \neq 0}} f(|p+x|^2), \quad L \in \mathcal{L}_d, \quad x \in \mathbb{R}^d.$$

First, it is clear that $x \mapsto E_f[L + x]$ is periodic with respect to L . Therefore, we will write that $x = x'$ modulo L if and only if $x - x' \in L$, and in particular $E_f[L + x] = E_f[L + x']$.

Only few methods are available to carry out the minimization of E_f . Historically, the first one consists to parametrize all the lattices of $\mathcal{L}_d(1)$ in an Euclidean fundamental domain $\mathcal{D}_d \subset \mathbb{R}^{\frac{d(d+1)}{2}-1}$ (see, e.g., [50, Sect. 1.4]) and to study the variations of the energy in \mathcal{D}_d . It has been done in dimension 2 for showing the optimality of the triangular lattice A_2 at fixed density for the Epstein zeta function [20, 28, 29, 44] and the lattice theta function [39], respectively, defined for $s > d$ and $\alpha > 0$ by

$$\zeta_L(s) := \sum_{p \in L \setminus \{0\}} \frac{1}{|p|^s}, \quad \text{and} \quad \theta_L(\alpha) := \sum_{p \in L} e^{-\pi\alpha|p|^2}. \tag{1.3}$$

In particular, a simple consequence of Montgomery’s result [39] for the lattice theta function is the universal optimality among lattices of A_2 (see, e.g., [4, Prop. 3.1]). Other consequences of the universal optimality of A_2 among lattices have been derived for other potentials (including the Lennard-Jones one) [4, 7, 14, 15] as well as masses interactions [11]. Furthermore, new interesting and general consequences of universal optimality will be derived in this paper, including a sufficient condition for the minimality of a universal minimizer at fixed density (see Theorem 2.9).

This variational method is also the one we have recently chosen in [9] for showing the maximality of A_2 in $\mathcal{L}_2(1)$ —and conjectured the same results in dimensions $d \in \{8, 24\}$ for the lattices E_8 and Λ_{24} —for the alternating and centered lattice theta function, respectively, defined, for all $\alpha > 0$, by

$$\theta_L^\pm(\alpha) := \sum_{p \in L} \varphi_\pm(p) e^{-\pi\alpha|p|^2}, \quad \text{and} \quad \theta_L^c(\alpha) := \sum_{p \in L} e^{-\pi\alpha|p+c_L|^2}, \tag{1.4}$$

where $L = \bigoplus_{i=1}^d \mathbb{Z}u_i$, $\{u_i\}_i$ being a Minkowski (reduced) basis of L (see, e.g., [50, Sect. 1.4.2]), $\varphi_\pm(p) := \sum_{i=1}^d m_i$ for $p = \sum_{i=1}^d m_i u_i$, $m_i \in \mathbb{Z}$ for all i , and $c_L = \frac{1}{2} \sum_i u_i$ is the center of its unit cell Q_L . In particular, the alternate lattice theta function $\theta_L^\pm(\alpha)$ can be viewed as the Gaussian interaction energy of a lattice L with an alternating distribution of charges ± 1 , which can be itself seen as the energy once we have removed 2 times the union of sublattices $\cup_{i=1}^d (L + u_i)$ from the original lattice L . This result shows another example of universal optimality—we will call it *universal maximality*—among lattices, i.e., the maximality of A_2 in $\mathcal{L}_2(1)$ for the energies E_f^\pm and E_f^c defined by

$$E_f^\pm[L] := \sum_{p \in L \setminus \{0\}} \varphi_\pm(p) f(|p|^2), \quad \text{or} \quad E_f^c[L] := \sum_{p \in L} f(|p+c_L|^2), \tag{1.5}$$

where $f \in \mathcal{F}_d^{cm}$. This kind of problem was actually our first motivation for investigating the effects of periodic arrays of defects on lattice energy minimizers, since removing two times the sublattices $2L + u_1$ and $2L + u_2$ totally inverses the type of optimality among lattices. Furthermore, this maximality result will also be used in Theorem 2.4, applied—in the general case of a universal maximizer L_d^\pm for E_f^\pm in any dimension where this property could be shown—for other potentials $\mathcal{F}_d \setminus \mathcal{F}_d^{cm}$ in Theorem 2.11 and compared with other optimality results in Sect. 3.2.

The second method for showing such optimality result is based on the Cohn–Elkies linear programming bound that was successfully used for showing the best packing results in dimensions 8 and 24 for E_8 and Λ_{24} in [23, 53], as well as their universal optimality among all periodic configurations in [24]. As in the two-dimensional case, many consequences of these optimality results have been shown for other potentials [14, 40] and masses interactions [8].

1.2. Problem Studied in This Paper and Connection to Material Science

The goal of this work is to investigate the effect on the minimizers of E_f when we change, given a lattice $L \subset \mathcal{L}_d$ and $K \subset \mathbb{N} \setminus \{1\}$, a certain real number $a_k \neq 0$ of integer sublattices kL , $k \in K$, in the original lattice, and where the lattices kL might be shifted by a finite number of lattice points $L_k := \{p_{i,k}\}_{i \in I_k} \subset L$ for some finite set I_k . Writing

$$\begin{aligned} \kappa &:= \{K, A_K, P_K\}, \quad K \subset \mathbb{N} \setminus \{1\}, \quad A_K = \{a_k\}_{k \in K} \subset \mathbb{R}^*, \\ P_K &= \bigcup_{k \in K} L_k, \quad L_k = \{p_{i,k}\}_{i \in I_k} \subset L, \end{aligned} \tag{1.6}$$

the new energy E_f^κ we consider, defined for $f \in \mathcal{F}_d$ and κ as in (1.6) and such that the following sum on K is absolutely convergent, is given by

$$E_f^\kappa[L] := E_f[L] - \sum_{k \in K} \sum_{i \in I_k} a_k E_f[p_{i,k} + kL]. \tag{1.7}$$

It is clear that we will never have $0 \in p_{i,k} + kL$; otherwise, the shifted case would be a non-shifted one. We also choose the following convention: $I_k = \emptyset$ implies that the sum over I_k in (1.7) does not appear for this particular $k \in K$. In particular, in the non-shifted case, i.e., $P_K = \emptyset$, then

$$E_f^\kappa[L] = E_{f_\kappa}[L], \quad \text{where} \quad f_\kappa(r) := f(r) - \sum_{k \in K} a_k f(k^2 r). \tag{1.8}$$

It is very important to notice that, once a sublattice is changed from the original lattice L , then the energy E_f^κ we study in this paper is no longer the total energy per point of the system but only the interaction energy between the origin and the charged lattice structure. That is why we called E_f^κ a ‘building block’ of the total energy that must consist in a finite sum of such lattice energies taking into account the interaction energy of each point with the rest of the structure. We already know that minimizing this kind of sum is very delicate (see, e.g., [10]) excepted in very special cases. Our goal can be considered as modest but at least a complete picture of the effect of periodic arrays of defects can be found in several cases and interesting properties can

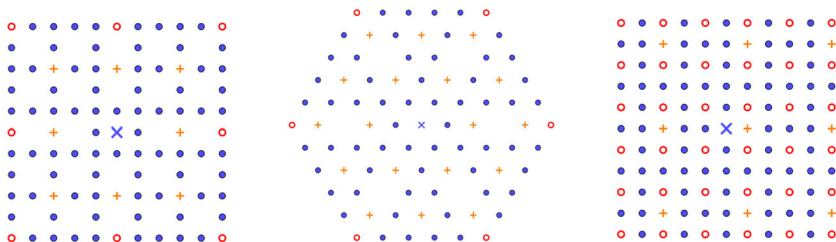


FIGURE 2. Mathematical examples of periodic array of defects performed on a patch of the square lattice \mathbb{Z}^2 (left and right) and the triangular lattice A_2 (middle). The cross blue times represents the origin O of \mathbb{R}^2 . The points marked by blue point are the original points of the lattice, whereas the points marked by orange plus and red point are substitutional defects of charge $1 - a_k$ for some $a_k \in \mathbb{R}^* \setminus \{1\}$ and some $k \in K := \{2, 3, 4, 5\}$. The missing lattice points are the vacancy defects. The patch on the right contains two shifted periodic arrays of defects (color figure online)

be derived for important specific potentials as power laws and Lennard-Jones potentials.

Since we are interested in the effects of defects on lattice energy ground states, we therefore want to derive conditions on κ and f such that E_f and E_f^κ have the same minimizers in \mathcal{L}_d or $\mathcal{L}_d(V)$ for fixed $V > 0$. In particular, we also want to know whether the universal minimality among lattices of a lattice L_d is conserved while removing or substituting integer sublattices. This a natural step for investigating the robustness of the optimality results stated in the previous section of this paper when the interaction potential is completely monotone or, for instance, of Lennard-Jones type. Furthermore, it is also the opportunity to derive new applications and generalizations of the methods recently developed in [4, 9, 14] for more ‘exotic’ ionic-like structures.

Replacing integer sublattices as described above can be interpreted and classified in two relevant cases in material science:

1. If $a_k = 1$, then removing only once the sublattice kL from L creates a periodic array of vacancies (also called periodic Schottky defects [51, Sect. 3.4.3]);
2. If $a_k \neq 1$, then ‘removing’ a_k times the sublattice kL from L creates a periodic array of substitutional defects (also called impurities), where the original lattice points (initially with charges $+1$) are replaced by points with ‘charges’ (or ‘weights’) $1 - a_k \neq 0$.

In Fig. 2, we have constructed three examples of two-dimensional lattices with periodic arrays of defects which certainly do not exist in the real world. In contrast, Fig. 3 shows two important examples of crystal structures arising in nature: the Kagome lattice and the rock-salt structure. These examples are discussed further in Sect. 3.

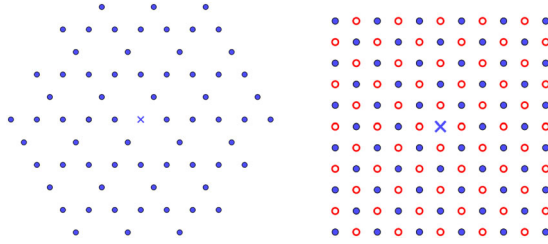


FIGURE 3. Two examples of 2d lattices patches with a periodic array of defect arising in nature. The left-hand structure is the Kagome lattice obtained by removing from the triangular lattice A_2 the sublattice $2A_2 + (1, 0) + (1/2, \sqrt{3}/2)$. It appears to be a layer of the jarosite. The right-hand structure is the 2d rock-salt structure obtained by removing from the square lattice \mathbb{Z}^2 two times the sublattices $2\mathbb{Z}^2 + (1, 0)$ and $2\mathbb{Z}^2 + (0, 1)$ in such a way that particles of opposite signs ± 1 alternate (blue point and red point correspond, respectively, to charges of signs 1 and -1). It is itself a layer of the three-dimensional rock-salt structure NaCl (color figure online)

While the substitutional defects case has different interpretations and applications in terms of optimal multi-component (ionic) crystals (see, e.g., Sect. 3.2), the vacancy case is also of interest when we look for accelerating the computational time for checking numerically the minimality of a structure. Indeed, if the minimizer does not change once several periodic arrays of points are removed from all lattices, then a computer will be faster to check this minimality. This is of practical relevance in particular in low dimensions since the computational time of such lattice energies, which grows exponentially with the dimension, are extremely long in dimension $d \geq 8$ —even with the presence of periodic arrays of vacancies—and shows how important are rigorous minimality results in these cases.

Furthermore, from a physics point of view, it is well known (see, e.g., [51]) that point defects play an important role in crystal properties. As explained in [1]: ‘Crystals are like people, it is the defects in them which tend to make them interesting.’ For instance, they reduce the electric and thermal conductivity in metals and modify the colors of solids and their mechanical strength. We also notice that substitutional defects control the electronic conductivity in semi-conductors, whereas the vacancies control the diffusion and the ionic conductivity in a solid. In particular, there is no perfect crystal in nature and it is then interesting and physically relevant to study optimality results for periodic systems with defects, in particular for models at positive temperature where the number of vacancies per unit volume increases exponentially with the temperature (see, e.g., [51, Sect. 3.4.3]). Notice that the raise of temperature also creates another kind of defects called self-interstitial—i.e., the

presence of extra atoms out of lattice sites—but they are known to be negligible (at least if they are of the same type than the solid's atoms) compared to the vacancies when disorder appears, excepted for Silicon.

Plan of the Paper Our main results are presented in Sect. 2, whereas their proofs are postponed to Sect. 4. Many applications of our results are discussed in Sect. 3, including explicit examples of minimality results for the Kagome lattice and other ionic structures.

2. Statement of the Main Results

2.1. On the Minimality of a Universal Optimizer

We start by recalling the notion of universal optimality among lattices as defined by Cohn and Kumar [22].

Definition 2.1 (*Universal optimality among lattices*). Let $d \geq 2$. We say that L_d is universally optimal in $\mathcal{L}_d(1)$ if L_d is a minimizer of E_f defined by (1.2) in $\mathcal{L}_d(1)$ for any $f \in \mathcal{F}_d^{cm}$.

Remark 2.1 (Universally optimal lattices). We recall again that the only known universally optimal lattices in dimension $d \geq 2$ are A_2 (see [39]), E_8 and the Leech lattice Λ_{24} (see [24]) in dimensions $d \in \{2, 8, 24\}$. It is also shown in [46, p. 117] that there is no such universally optimal lattice in dimension $d = 3$. There are also clear indications (see [14, Sect. 6.1]) that the space of functions for which the minimality at all the scales of L_d holds is much larger than \mathcal{F}_d^{cm} .

Before stating our results, notice that all of them are stated in terms of global optimality, but could be rephrased for showing local optimality properties. This is important, in particular, in dimensions $d = 3$ where only local minimality results are available for E_f (see, e.g., [6]) and can be generalized for energies of type E_f^κ , ensuring the local stability of certain crystal structures.

We now show that the universal optimalities among lattices in dimension $d \in \{2, 8, 24\}$ proved in [24, 39] are not conserved in the non-shifted case once we only removed a single integer sublattice a positive number $a_k > 0$ of times, whereas they are conserved when $a_k < 0$.

Theorem 2.2 (Conservation of universal optimalities—non-shifted case). *Let f be defined by $f(r) = e^{-\pi\alpha r}$, $\alpha > 0$. For all $d \in \{2, 8, 24\}$, all $k \in \mathbb{N} \setminus \{1\}$, all $a_k > 0$ and $\kappa = \{\{k\}, \{a_k\}, \emptyset\}$, there exists α_d such that for all $\alpha \in (0, \alpha_d)$, A_2 , E_8 and the Leech lattice Λ_{24} are not minimizers of E_f^κ in $\mathcal{L}_d(1)$.*

Furthermore, for any $d \in \{2, 8, 24\}$, for any $K \subset \mathbb{N} \setminus \{1\}$, any $A_K = \{a_k\}_{k \in K} \subset \mathbb{R}_-$ and $\kappa = \{K, A_K, \emptyset\}$, A_2 , E_8 and the Leech lattice Λ_{24} are the unique minimizers of E_f^κ in $\mathcal{L}_d(1)$ for all $\alpha > 0$.

Remark 2.3 (Generalization to 4 designs). The non-optimality result in Theorem 2.2 is obtained by using the Taylor expansion of the theta function found by Coulangeon and Schürmann [26, Eq. (21)]. Therefore, the result is actually generalizable to any universal optimal lattice L_d such that all its layers (or

shells) are 4 designs, i.e., such that for all $r > 0$ with $\{\partial B_r \cap L_d\} \neq \emptyset$, B_r being the ball centered at the origin and with radius r , and all polynomial P of degree up to 4 we have

$$\frac{1}{|\partial B_r|} \int_{\partial B_r} P(x) dx = \frac{1}{\#\{\partial B_r \cap L_d\}} \sum_{x \in \partial B_r \cap L_d} P(x).$$

We now present a sufficient condition on P_K such that the triangular lattice is universally optimal in $\mathcal{L}_2(1)$ for E_f^κ . This result is based on our recent work [9] where we have proved the maximality of A_2 in $\mathcal{L}_2(1)$ for the centered lattice theta functions, i.e., $L \mapsto \theta_{L+c_L}(\alpha)$, where c_L is the center of the unit cell Q_L (see also Remark 2.12).

Theorem 2.4 (Conservation of universal optimality—2d shifted case). *Let $d = 2$ and $\kappa = \{K, A_K, P_K\}$ be as in (1.6) where $A_K \subset \mathbb{R}_+$, and be such that*

$$\forall k \in K, \forall i \in I_k, \quad \frac{P_{i,k}}{k} = c_L \text{ modulo } L, \quad L = \mathbb{Z}u_1 \oplus \mathbb{Z}u_2, \quad c_L := \frac{u_1 + u_2}{2}, \tag{2.1}$$

where Q_L is the unit cell of L defined by (1.1) with a Minkowski basis $\{u_1, u_2\}$ and its center c_L . Then, for all $f \in \mathcal{F}_2^{c_m}$, A_2 is the unique minimizer of E_f^κ in $\mathcal{L}_2(1)$.

Example 2.5. Theorem 2.4 holds in a particularly simple case, when $k = 2$ and $p_{i,2} = u_1 + u_2 \in L$.

Remark 2.6 (Conjecture in dimensions $d \in \{8, 24\}$.) Theorem 2.4 is based on the fact that A_2 has been shown to be the unique maximizer of E_f^c defined in (1.5) in $\mathcal{L}_d(1)$ for any $f \in \mathcal{F}_d^{c_m}$ (see also Remark 2.12). As discussed in [9], we believe that this result still holds in dimensions 8 and 24 for E_8 and the Leech lattice Λ_{24} , as well as Theorem 2.4.

Remark 2.7 (Phase transition for the minimizer in the Gaussian case—numerical observation). In the non-universally optimal case of Theorem 2.2 and the shifted case satisfying (2.1), numerical investigations suggest that the minimizer of E_f^κ exhibits a phase transition as the density decreases.

Non-shifted case Let us consider the example $f(r) = e^{-\pi\alpha r}$ given in Theorem 2.2 (i.e., $f(r^2)$ is a Gaussian function) and $f_\kappa(r) = e^{-\pi\alpha r} - 0.1e^{-2\pi\alpha r}$ (defined by (1.8)), $\kappa := \{\{2\}, \{0.1\}, \emptyset\}$, corresponding to removing $a_2 = 0.1$ times the sublattice $2L$ ($k = 2$) from the original lattice L . In dimension $d = 2$, we numerically observe an interesting phase transition of type ‘triangular–rhombic–square–rectangular’ for the minimizer of E_f^κ in $\mathcal{L}_2(1)$ as α (which plays the role of the inverse density here) increases.

Shifted case with $a_k < 0$ Let us assume that $K = \{2\}$, $A_K := \{a_2 < 0\}$, $I_2 = \{1\}$ and $p_{1,2} = u_1 + u_2$ in such a way that (2.1) is satisfied. If we consider $f(r) = e^{-\pi\alpha r}$, then for all the negative parameters a_2 we have chosen, the minimizer of $E_f^\kappa[L] := \theta_L(\alpha) + |a_2|\theta_{L+c_L}(\alpha)$ in $\mathcal{L}_2(1)$ numerically shows the

same phase transition of type ‘triangular–rhombic–square–rectangular’ as α increases.

This type of phase transition seems to have a certain universality in dimension 2 since it was also observed for Lennard-Jones energy [5], Morse energy [7], Madelung-like energies [10] and proved for 3-block copolymers [36] and two-component Bose–Einstein condensates [37] by Wei et al..

Remark 2.8 (Optimality of \mathbb{Z}^d in the orthorhombic case). Another type of universal optimality is known in the set of orthorhombic lattices, i.e., the lattice L which can be represented by an orthogonal basis. As proved by Montgomery in [39, Thm. 2], the cubic lattice \mathbb{Z}^d is universally minimal among orthorhombic lattices of unit density in any dimension (see also [10, Rmk. 3.1]). The proof of Theorem 2.2 can be easily adapted to show the same optimality result for \mathbb{Z}^d among orthorhombic lattices of unit density. Furthermore, it has also been shown (see, e.g., [13, Prop. 1.4]) that \mathbb{Z}^d is the unique maximum of $L \mapsto E_f[L + c_L]$ among orthorhombic lattices of fixed density for any $f \in \mathcal{F}_d^{cm}$. Therefore, the proof of Theorem 2.4 can be also easily adapted in this orthorhombic case in order to show the universal optimality of \mathbb{Z}^d in this particular shifted case. Moreover, all the next results involving any universally optimal lattice can be rephrased for \mathbb{Z}^d in the space of orthorhombic lattices. Examples of applications of such result will be discussed in Sect. 3.2.

We now give a general criterion that ensures the conservation of an universal optimizer’s minimality for E_f^κ .

Theorem 2.9 (General criterion for minimality conservation—non-shifted case). *Let $d \geq 2$, $\kappa = \{K, A_K, \emptyset\}$ be as in (1.6) (possibly empty) where $A_K \subset \mathbb{R}_+$, and L_d be universally optimal in $\mathcal{L}_d(1)$. Furthermore, let $f \in \mathcal{F}_d$ be such that $d\mu_f(t) = \rho_f(t)dt$ and f_κ be defined by (1.8). Then:*

1. For any κ , we have $f_\kappa(r) = \int_0^\infty e^{-rt} d\mu_{f_\kappa}(t)$ where

$$d\mu_{f_\kappa}(t) = \rho_{f_\kappa}(t)dt, \quad \rho_{f_\kappa}(t) = \rho_f(t) - \sum_{k \in K} \frac{a_k}{k^2} \rho_f\left(\frac{t}{k^2}\right).$$

2. The following equivalence holds: $f_\kappa \in \mathcal{F}_d^{cm}$ if and only if

$$\forall t > 0, \quad \rho_f(t) \geq \sum_{k \in K} \frac{a_k}{k^2} \rho_f\left(\frac{t}{k^2}\right); \tag{2.2}$$

3. If (2.2) holds, then L_d is the unique minimizer of E_f^κ in $\mathcal{L}_d(1)$.

4. If there exists $V > 0$ such that for a.e. $y \geq 1$ there holds

$$g_V(y) := \rho_{f_\kappa}\left(\frac{\pi y}{V^{\frac{2}{d}}}\right) + y^{\frac{d}{2}-2} \rho_{f_\kappa}\left(\frac{\pi}{V^{\frac{2}{d}}y}\right) \geq 0, \tag{2.3}$$

then $V^{\frac{1}{d}}L_d$ is the unique minimizer of E_f^κ in $\mathcal{L}_d(V)$.

The fourth point on Theorem 2.9 generalizes our two-dimensional result [4, Thm. 1.1] to any dimension and with possible periodic arrays of defects. It

is an important result since only few minimality results for E_f are available for non-completely monotone potentials $f \in \mathcal{F}_d \setminus \mathcal{F}_d^{cm}$, and this is also the first result of this kind for charged lattices (i.e., when the particles are not of the same kind). Condition (2.3) has been used in dimension $d = 2$ in [4, 7] for proving the optimality of a triangular lattice at fixed density for non-convex sums of inverse power laws, differences of Yukawa potentials, Lennard-Jones potentials and Morse potentials and we expect the same property to hold in higher dimension. In Theorem 2.17, we will give an example of such application in any dimension d by applying the fourth point of Theorem 2.9 to Lennard-Jones-type potentials. We now add a very important remark concerning the adaptation of the fourth point of Theorem 2.9 in the general periodic case, i.e., for crystallographic point packings (see [2, Def. 2.5]).

Remark 2.10 (Crystallization at fixed density as a consequence of Cohn–Kumar Conjecture). When $\kappa = \emptyset$, i.e., all the particles are present and of the same kind, the proof of point 4. of Theorem 2.9 admits a straightforward adaptation in the periodic case, i.e., among all configurations $\mathcal{C} = \bigcup_{i=1}^N (\Lambda + v_k) \in \mathcal{S}$ being Λ -periodic of unit density, where $\Lambda \in \mathcal{L}_d$, i.e., such that $|\Lambda| = N$, and with a f -energy defined for $V > 0$ by

$$E_f[V^{\frac{1}{d}}\mathcal{C}] := \frac{1}{N} \sum_{j,k=1}^N \sum_{x \in \Lambda \setminus \{v_k - v_j\}} f\left(V^{\frac{2}{d}}|x + v_k - v_j|^2\right).$$

Using again the representation of f as a superposition of Gaussians combined with the Jacobi transformation formula (see the proof of Theorem 2.9), the same condition (2.3) ensures the crystallization on L_d at fixed density once we know its universal optimality in the set of all periodic configurations with fixed density V^{-1} . This result is in the same spirit as the one derived by Petrache and Serfaty in [40] for Coulomb and Riesz interactions. In dimensions $d \in \{8, 24\}$, (2.3) implies the crystallization on E_8 and Λ_{24} at fixed density V^{-1} as a consequence of [24], whereas in dimension $d = 2$ it is conjectured by Cohn and Kumar in [22] that the same holds on the triangular lattice. It is in particular true for the Lennard-Jones potential at high density as a simple application of our Theorem 2.17.

Using exactly the same arguments as the fourth point of Theorem 2.9, we show the following result which gives a sufficient condition on an interaction potential f for a universal maximizer L_d^\pm of $\theta_L^\pm(\alpha)$ to be optimal for E_f^\pm , where

$$\theta_L^\pm(\alpha) := \sum_{p \in L} \varphi_\pm(p) e^{-\pi\alpha|p|^2}, \quad \text{and} \quad E_f^\pm[L] := \sum_{p \in L \setminus \{0\}} \varphi_\pm(p) f(|p|^2), \quad (2.4)$$

with $L = \bigoplus_{i=1}^d \mathbb{Z}u_i$, $\{u_1, \dots, u_d\}$ being its Minkowski basis, and $\varphi_\pm(p) = \sum_{i=1}^d m_i$ for $p = \sum_{i=1}^d m_i u_i$, $m_i \in \mathbb{Z}$ for all i . Remark that $E_f^\pm = E_f^\kappa$ when $\kappa = \{\{2\}, \{2\}, \{u_1, \dots, u_d\}\}$, $L = \bigoplus_{i=1}^d \mathbb{Z}u_i$. In particular, it holds for the triangular lattice A_2 as a simple application of our main result in [9].

Theorem 2.11 (Maximality of a universal maximizer for θ_L^\pm —Shifted case). *Let $d \geq 2$, $V > 0$, $\kappa = \{\{2\}, \{2\}, \{u_1, \dots, u_d\}\}$, where a generic lattice is written $L = \bigoplus_{i=1}^d \mathbb{Z}u_i$, $\{u_1, \dots, u_d\}$ being its Minkowski basis, and L_d^\pm be the unique maximizer of $\theta_L^\pm(\alpha)$, defined by (2.4), in $\mathcal{L}_d(1)$ and for all $\alpha > 0$. If $f \in \mathcal{F}_d$ satisfies (2.3), then $V^{\frac{1}{d}}L_d^\pm$ is the unique maximizer of E_f^κ (equivalently of E_f^\pm defined by (2.4)) in $\mathcal{L}_d(V)$.*

Remark 2.12 (Adaptation to shifted f -energy). We believe that Theorem 2.11 also holds for E_8 and Λ_{24} (see [9, Conj. 1.3] and Remark 2.6). Furthermore, the same kind of optimality result could be easily derived for any energy shifted energy of type $L \mapsto E_f[L+c]$ where $c \in Q_L$ is fixed as a function of the vectors in the Minkowski basis $\{u_i\}$ and when one knows a universal minimizer or maximizer for $L \mapsto E_f[L+c]$, $f \in \mathcal{F}_d^{cm}$. However, no other result concerning any optimality of a lattice for such kind of energy is currently available when $c \notin \{L, c_L\}$.

The rest of our results are all given in the non-shifted case $P_K = \emptyset$. It is indeed a rather difficult task to minimize the sum of shifted and/or non-shifted energies of type E_f . Very few results are available and the recent work by Luo and Wei [37] has shown the extreme difficulty to obtain any general result for completely monotone function f . Shifting the lattices by a non-lattice point which is not the center c_L appears to be deeply more tricky in terms of energy optimization.

We remark that, since \mathcal{F}_d^{cm} is not stable by difference, it is not totally surprising that Theorem 2.2 holds. Furthermore, identifying the largest space of all functions f such that E_f is uniquely minimized by L_d in $\mathcal{L}_d(1)$ seems to be very challenging (see [14]). Therefore, a natural question in order to identify a large class of potentials f such that the minimality of an universal optimizer L_d holds for E_f^κ is the following: What are the completely monotone potentials $f \in \mathcal{F}_d^{cm}$ satisfying (2.2), i.e., such that $f_\kappa \in \mathcal{F}_d^{cm}$? The following corollary of Theorem 2.9 gives an example of such potentials, where we define, for $s > 0$ and any $A_K = \{a_k\}_{k \in K}$, $K \subset \mathbb{N} \setminus \{1\}$,

$$L(A_K, s) := \sum_{k \in K} \frac{a_k}{k^s}. \tag{2.5}$$

Notice that the notation of (2.5) is inspired by the one of Dirichlet L-series that are generalizing the Riemann zeta function (see, e.g., [21, Chap. 10]). For us, the arithmetic function appearing in a Dirichlet series is simply replaced by A_K and can be finite.

Corollary 2.13 (Minimality conservation for special f —non-shifted case). *Let $d \geq 2$ and $f \in \mathcal{F}_d^{cm}$ be such that $d\mu_f(t) = \rho_f(t)dt$ and ρ_f be an increasing function on \mathbb{R}_+ . Let $\kappa = \{K, A_K, \emptyset\}$ be as in (1.6) where $A_K = \{a_k\}_{k \in K} \subset \mathbb{R}_+$ and be such that $L(A_K, s)$ defined by (2.5) satisfies $L(A_K, 2) \leq 1$. If L_d is universally optimal in $\mathcal{L}_d(1)$, then L_d is the unique minimizer of E_f^κ in $\mathcal{L}_d(1)$.*

Example 2.14 (Potentials satisfying the assumptions of Corollary 2.13). There are many examples of potentials f such that Corollary 2.13 holds. For instance,

this is the case for the parametrized potential $f = f_{\sigma,s}$ defined for all $r > 0$ by $f_{\sigma,s}(r) = \frac{e^{-\sigma r}}{r^s}$, $\sigma > 0$, $s > 1$, since $d\mu_{f_{\sigma,s}}(t) = \frac{(t-\sigma)^{s-1}}{\Gamma(s)} \mathbb{1}_{[\sigma,\infty)}(t)dt$ and $t \mapsto \frac{(t-\sigma)^{s-1}}{\Gamma(s)} \mathbb{1}_{[\sigma,\infty)}(t)$ are increasing functions on \mathbb{R}_+ . Notice that the inverse power law $f(r) = r^{-s}$ with exponent $s > d/2 \geq 1$ (if $\sigma = 0$) and the Yukawa potential $f(r) = e^{-\sigma r} r^{-1}$ with parameter $\sigma > 0$ (if $s = 1$) are special cases of $f_{\sigma,s}$.

2.2. The Inverse Power Law and Lennard-Jones Cases

In this subsection, we restrict our study to combinations of inverse power laws, since they are the building blocks of many interaction potentials used in molecular simulations (see, e.g., [34]). Their homogeneity simplifies a lot the energy computations and allows us to give a complete picture of the periodic arrays of defects effects with respect to the values of L defined by (2.5).

In the following result, we show that the values of $L(A_K, 2s)$ plays a fundamental role in the minimization of E_f^κ when f is an inverse power law.

Theorem 2.15 (The inverse power law case—non-shifted case). *Let $d \geq 2$ and $f(r) = r^{-s}$ where $s > d/2$. Let $\kappa = \{K, A_K, \emptyset\}$ be as in (1.6) and be such that $L(A_K, 2s)$ defined by (2.5) is absolutely convergent. We have:*

1. *If $L(A_K, 2s) < 1$, then L_0 is a minimizer of $L \mapsto \zeta_L(2s)$ in $\mathcal{L}_d(1)$ if and only if L_0 is a minimizer of E_f^κ in $\mathcal{L}_d(1)$.*
2. *If $L(A_K, 2s) > 1$, then L_0 is a minimizer of $L \mapsto \zeta_L(2s)$ in $\mathcal{L}_d(1)$ if and only if L_0 is a maximizer of E_f^κ in $\mathcal{L}_d(1)$.*

In particular, for any $K \subset \mathbb{N} \setminus \{1\}$, if $a_k = 1$ for all $k \in K$, then $L \mapsto \zeta_L(2s)$ and E_f^κ have the same minimizers in $\mathcal{L}_d(1)$.

Example 2.16 (Minimizers of the Epstein zeta function). In dimensions $d \in \{2, 8, 24\}$, the minimizer L_0 of $L \mapsto \zeta_L(2s)$ in $\mathcal{L}_d(1)$ is, respectively, A_2 , E_8 and Λ_{24} as consequences of [24,39]. In dimension $d = 3$, Sarnak and Strömbergsson have conjectured in [46, Eq. (44)] that the face-centered cubic lattice D_3 (see Fig. 1) is the unique minimizer of $L \mapsto \zeta_L(2s)$ in $\mathcal{L}_3(1)$ if $s > 3/2$.

Many applications of point 4. of Theorem 2.9 can then be shown for non-convex sums of inverse power laws, differences of Yukawa potentials or Morse potentials by following the lines of [4]. In this paper, we have chosen to focus on Lennard-Jones-type potentials since it is possible to have a complete description of the effect of non-shifted periodic arrays of vacancies using the homogeneity of the Epstein zeta functions. It is also known that Lennard-Jones-type potentials play an important role in molecular simulation (see, e.g., [4, Sect. 6.3] and [34, Sect. 5.1.2]).

In our last results, we define the Lennard-Jones-type potential by

$$f(r) = \frac{c_2}{r^{x_2}} - \frac{c_1}{r^{x_1}} \quad \text{where} \quad (c_1, c_2) \in (0, \infty), \quad x_2 > x_1 > d/2, \quad (2.6)$$

which is a prototypical example of function where μ_f is not non-negative everywhere, and a difference of completely monotone functions. We discuss the optimality of a universally optimal lattice L_d for E_f^κ with respect to the values

of $L(A_K, 2x_i)$, $i \in \{1, 2\}$ as well as the shape of the global minimizer of E_f^κ , i.e., its equivalence class in \mathcal{L}_d modulo rotation and dilation (as previously defined in [14]).

Theorem 2.17 (The Lennard-Jones case—non-shifted case). *Let $d \geq 2$, f be defined by (2.6) and $\kappa = \{K, A_K, \emptyset\}$ be as in (1.6) (possibly empty) and be such that $L(A_K, 2x_i)$, $i \in \{1, 2\}$ defined by (2.5) are absolutely convergent. Let L_d be universally optimal in $\mathcal{L}_d(1)$. Then:*

1. *If $L(A_K, 2x_2) < L(A_K, 2x_1) < 1$, then for all $V > 0$ such that*

$$V \leq V_\kappa := \pi^{\frac{d}{2}} \left(\frac{c_2(1 - L(A_K, 2x_2))\Gamma(x_1)}{c_1(1 - L(A_K, 2x_1))\Gamma(x_2)} \right)^{\frac{d}{2(x_2 - x_1)}},$$

the lattice $V^{\frac{1}{d}}L_d$ is the unique minimizer of E_f^κ in $\mathcal{L}_d(V)$ and there exists $V_1 > 0$ such that it is not a minimizer of E_f^κ for $V > V_1$. Furthermore, the shape of the minimizer of E_f and E_f^κ are the same in \mathcal{L}_d .

2. *If $L(A_K, 2x_1) > L(A_K, 2x_2) > 1$, then E_f^κ does not have any minimizer in \mathcal{L}_d and for all $V < V_\kappa$, $V^{\frac{1}{d}}L_d$ is the unique maximizer of E_f^κ in $\mathcal{L}_d(V)$.*
3. *If $L(A_K, 2x_1) > 1 > L(A_K, 2x_2)$, then E_f^κ does not have any minimizer in \mathcal{L}_d but $V^{\frac{1}{d}}L_d$ is the unique minimizer of E_f^κ in $\mathcal{L}_d(V)$ for all $V > 0$.*

Remark 2.18 (Increasing of the threshold value V_κ .) The fact that $1 - L(A_K, 2x_2) > 1 - L(A_K, 2x_1)$ implies that the threshold value V_κ is larger in the $\kappa \neq \emptyset$ case than in the case without defect $\kappa = \emptyset$. The same is expected to be true for any non-convex sum of inverse power law with a positive main term as $r \rightarrow 0$ (see [4, Prop. 6.4] for a two-dimensional example in the no-defect case $\kappa = \emptyset$). It is also totally straightforward to show that $V_\kappa \rightarrow V_\emptyset$ as $\min K$ tend to $+\infty$.

Remark 2.19 (Global minimality of A_2 among lattices for Lennard-Jones-type potentials). In dimension $d = 2$, the triangular lattice $L_2 = A_2$ has been shown in [4, Thm. 1.2.2] to be the shape of the global minimizer of E_f in \mathcal{L}_2 when $\pi^{-x_2}\Gamma(x_2)x_2 < \pi^{-x_1}\Gamma(x_1)x_1$. Point 1. of Theorem 2.17 implies that the same holds when $L(A_K, 2x_2) < L(A_K, 2x_1) < 1$.

2.3. Conclusion

From all our results, we conclude that it is possible to remove or substitute several infinite periodic sets of points from all the lattices (i.e., an integer sublattices) and to conserve the already existing minimality properties, but only in a certain class of potentials or sublattices. Physically, it means that adding point defects to a crystal can be without any effect on its ground state if we assume the interaction between atoms to be well approximated by a pairwise potential (Born model [52]) and the sublattices to satisfy some simple properties. We give several examples in Sect. 3 and our result are the first known general results giving global optimality of ionic crystals. In particular, the Kagome lattice (see Fig. 3) is shown to be the global minimizer for the interaction energies discussed in this paper in the class of (potentially shifted) lattices $L \setminus 2L$ where $L \in \mathcal{L}_2(1)$. This is, as far as we know, the first results of

this kind for the Kagome lattice. We also believe that the results and techniques derived in this paper can be applied to other ionic crystals and other general periodic systems.

Furthermore, this paper also shows the possibility to check the optimality of a structure while ‘forgetting’ many points which, in a certain sense, do not play any role (vacancy case). This allow to simplify both numerical investigations—leading to a shorter computational time—and mathematical estimates for these energies. We voluntarily did not explore further this fact since it is only relevant in low dimensions because the computational time of such lattice sums is exponentially growing and gives unreachable durations in dimension $d \geq 4$ for computing many values of the energies, especially in dimensions $d \in \{8, 24\}$ where our global optimality results are applicable.

In dimension $d = 3$, i.e., where the everyday life real crystals exist, our results only apply—combined with the one from [6]—to the conservation of local minimality in the cubic lattices cases (\mathbb{Z}^3 , D_3 and D_3^*) for the Epstein zeta function, the lattice theta function and the Lennard-Jones-type energies. We believe that our result will find other very interesting applications in dimension 3 once global optimality properties will be shown for the lattice theta functions and the Epstein zeta functions (Sarnak–Strömbergsson conjectures [46]).

Even though the inverse power laws and Lennard-Jones cases have been completely solved here, we still ignore what is the optimal result that holds for ensuring the robustness of the universal optimality among lattices. An interesting problem would be to find a necessary condition for this robustness. Furthermore, we can also ask the following question: is it enough to study this kind of minimization problem in a (small) ball centered at the origin? In other words: can we remove all the points that are far enough from O and conserving the minimality results? Numerical investigations and Fig. 5 tend to confirm this fact, and a rigorous proof of such property would deeply simplify the analysis of such lattice energies.

3. Applications: The Kagome Lattice and Other Ionic Structures

We now give several examples of applications of our results. In particular, we identify interesting structures that are minimizers of E_f in classes of sparse and charged lattices.

3.1. The Kagome Lattice

Being the vertices of a trihexagonal tiling, this structure—which is actually not a lattice as we defined it in this paper—that we will write $K := A_2 \setminus 2A_2$ is the difference of two triangular lattices of scale ratio 2 (see Fig. 4). Some minerals—which display novel physical properties connected with geometrically frustrated magnetism—like jarosites and herbertsmithite contain layers having this structure (see [38] and references therein). We can therefore apply our results of Sect. 2 with $\kappa = \{\{2\}, \{1\}, \emptyset\}$ or $\kappa = \{\{2\}, \{1\}, \{u_1 + u_2\}\}$. The following optimality results for E_f in the class of lattices of the form $L \setminus 2L$

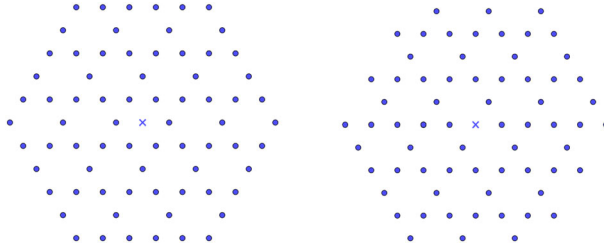


FIGURE 4. Two patches of the Kagome lattice. On the left, the origin O does not belong to K and is the center of one of the hexagons. On the right, O belongs to a shifted version $K + (1/2, -\sqrt{3}/2)$

(or $L \setminus (2L + u_1 + u_2)$ in the shifted case) are simple consequences of our results combined with the universal optimality of A_2 among lattices proved by Montgomery in [39]:

1. *Universal optimality of K .* Applying Theorem 2.4 to $\kappa = \{\{2\}, \{1\}, \{u_1 + u_2\}\}$, it follows that for all $f \in \mathcal{F}_2^{cm}$, the shifted Kagome lattice $K + (1/2, -\sqrt{3}/2)$ (see Fig. 4) is the unique minimizer of E_f among lattices of the form $L \setminus (2L + u_1 + u_2)$, where $L = \mathbb{Z}u_1 \oplus \mathbb{Z}u_2 \in \mathcal{L}_2(1)$.
2. *Minimality of K at all densities for certain completely monotone potentials.* A direct consequence of Theorem 2.9 is the following. For any completely monotone function $f \in \mathcal{F}_2^{cm}$ such that $d\mu_f(t) = \rho_f(t)dt$ and ρ_f is an increasing function, the Kagome lattice K is the unique minimizer of E_f among all the two-dimensional sparse lattices $L \setminus 2L$ where $L \in \mathcal{L}_2(1)$. This is the case, for instance, for $f = f_{\sigma,s}$ defined in Example 2.14, including the inverse power laws and the Yukawa potential.
3. *Optimality at high density for Lennard-Jones interactions.* Applying Theorem 2.17, we obtain its optimality at high density: if $f(r) = c_2r^{-x_2} - c_1r^{-x_1}$, $x_2 > x_1 > 1$ is a Lennard-Jones potential, then the unique minimizer of E_f at high density among all the two-dimensional sparse lattices $L \setminus 2L$, where L has fixed density, has the shape of K .
4. *Global optimality for Lennard-Jones interactions with small exponents.* Furthermore, using Theorem 2.17 and [4, Thm. 1.2.2] (see also Remark 2.19), we obtain the following interesting result in the Lennard-Jones potential case: if $\pi^{-x_2}\Gamma(x_2)x_2 < \pi^{-x_1}\Gamma(x_1)x_1$, then the unique global minimizer of E_f among all the possible sparse lattices $L \setminus 2L$ has the shape of K .

These are the first minimality results for K in a class of periodic configurations. We recall that a non-optimality result has also been derived by Grivopoulos [32] for Lennard-Jones potential in the case of free particles, and different attempts have been made for obtaining numerically or experimentally a Kagome structure as an energy ground state (see, e.g., [27, 33, 42]).

Remark 3.1. (The honeycomb lattice) We notice that the honeycomb lattice $H := A_2 \setminus \sqrt{3}A_2$, also constructed from the triangular lattice, does not belong

to the set of sparse lattices $L \setminus kL$, $k \in \mathbb{N}$. That is why no optimality result for H is included in this paper.

3.2. Rock-Salt Versus Other Ionic Structures

We recall that, in [9], we have shown with Faulhuber the universal optimality of the triangular lattice among lattices with alternating charges, i.e., the fact that A_2 uniquely maximizes

$$L \mapsto \theta_L^\pm(\alpha) := \sum_{p \in L} \varphi_\pm(p) e^{-\pi\alpha|p|^2} \quad \text{and} \quad \zeta_L^\pm(s) := \sum_{p \in L \setminus \{0\}} \frac{\varphi_\pm(p)}{|p|^s},$$

$$L = \mathbb{Z}u_1 \oplus \mathbb{Z}u_2, \tag{3.1}$$

in $\mathcal{L}_2(1)$, where, for all $p = mu_1 + nu_2$, $\varphi_\pm(p) := m + n$. Notice that the maximality result at all scales for the alternating lattice theta function is equivalent with the fact that A_2 maximizes

$$L \mapsto E_f^\kappa[L] := E_f[L] - 2E_f[2L + u_1] - 2E_f[2L + u_2],$$

where $\kappa := \{\{2\}, \{2\}, \{u_1, u_2\}\}$

in $\mathcal{L}_2(1)$ for any $f \in \mathcal{F}_2^{cm}$. It has been also proved in [13, Thm. 1.4] that \mathbb{Z}^d is the unique maximizer of the d -dimensional generalization of the two lattice energies $\theta_L^\pm(\alpha)$ and $\zeta_L^\pm(s)$ among d -dimensional orthorhombic (rectangular) lattices of fixed unit density, whereas it is a minimizer of the lattice theta functions and the Epstein zeta functions defined in (1.3). Furthermore, applying Theorem 2.9 in dimension $d = 2$ (resp. any d), we see that A_2 (resp. \mathbb{Z}^d) minimizes in $\mathcal{L}_2(1)$ (resp. among the orthorhombic lattices of unit density) the energy

$$E_f^\kappa[L] := \zeta_L(s) - 2\zeta_{kL}(s), \quad f(r) = r^{-s}, \quad K = \{k\}, \quad a_k = 2, \tag{3.2}$$

for all $s > d/2$. We remark that \mathbb{Z}^d , $d \in \{2, 3\}$ is also a saddle point (see [6, 39]) of E_f^κ in $\mathcal{L}_d(1)$. It is then interesting to see how the array of substitutional defects with charges -1 plays a totally different role for this energy (see also Figs. 5 and 6). This seems to confirm that the role of the nearest neighbors of the origin is fundamental, since they are actually the main terms of the energy when the potential is decreasing fast at infinity.

4. Proofs of the Main Results

We first show Theorem 2.2, i.e., the non-robustness of universal optimality results under non-shifted periodic arrays of defects.

Proof of Theorem 2.2. Let $\Lambda \in \{A_2, E_8, \Lambda_{24}\}$. We consider the potential $f(r) := e^{-\pi\alpha r}$ where $\alpha > 0$. For all $k \in \mathbb{N} \setminus \{1\}$, all $a_k > 0$ and all $L \in \mathcal{L}_d(1)$, we have, using the fact that $\theta_{kL}(\alpha) = \theta_L(k^2\alpha)$,

$$E_f^\kappa[L] = \theta_L(\alpha) - a_k\theta(k^2\alpha).$$

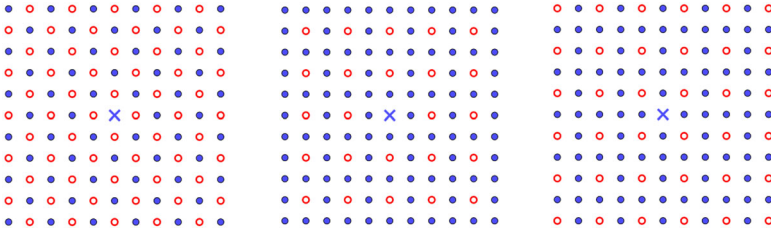


FIGURE 5. Three periodic arrays of defects on \mathbb{Z}^2 . Blue points are points with charges $+1$ and red points are with charges -1 . For the inverse power laws energies, the left-hand configuration is the unique maximizer among rectangular lattices of fixed density with alternation of charges, whereas the centered configuration is its unique minimizer with this distribution of charges among rectangular lattices. However, the configuration on the right is a saddle point of any energy on the form E_f , $f \in \mathcal{F}_2^{cm}$ in this class of charged configurations. For the two structures on the left, the same is true in higher dimension while generalizing the ionic-like distribution on orthorhombic lattices (color figure online)

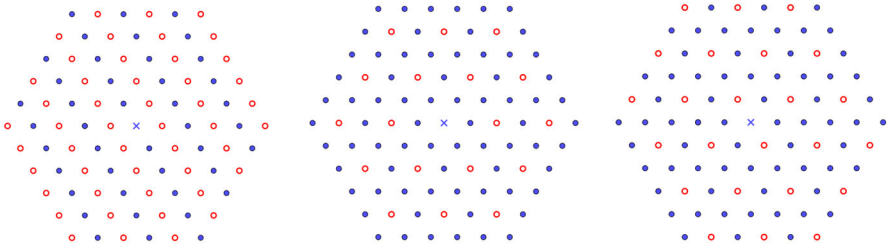


FIGURE 6. Three periodic arrays of defects on a patch of A_2 . Blue points are points with charges $+1$ and red points are with charges -1 . On the left, the triangular alternate configuration maximizes $\zeta_L^\pm(s)$ in $\mathcal{L}_2(1)$ with this alternation of charges, while the configuration in the middle minimizes the inverse power law energy in this class of charged lattices. The configuration on the right minimizes any energy on the form E_f , $f \in \mathcal{F}_2^{cm}$ in this class of charged configurations (color figure online)

Let us show that there exists α_d such that for all $0 < \alpha < \alpha_d$, Λ does not minimize E_f^κ in $\mathcal{L}_d(1)$. Indeed, we have the following equivalence: for all $L \in \mathcal{L}_d(1) \setminus \{\Lambda\}$, $E_f^\kappa[L] > E_f^\kappa[\Lambda]$ if and only if

$$\inf_{\substack{L \in \mathcal{L}_d(1) \\ L \neq \Lambda}} \frac{\theta_L(\alpha) - \theta_\Lambda(\alpha)}{\theta_L(k^2\alpha) - \theta_\Lambda(k^2\alpha)} > a_k. \tag{4.1}$$

Let us show that (4.1) does not hold for small α , and in particular that the left term tends to 0 as $\alpha \rightarrow 0$. We use Coulangeon and Schürmann’s work [26, Eq. (21)], in the lattice case, who derived the Taylor expansion of the theta function as $L \rightarrow \Lambda$ in $\mathcal{L}_d(1)$. We then obtain

$$\begin{aligned} \lim_{\substack{L \rightarrow \Lambda \\ L \neq \Lambda}} \frac{\theta_L(\alpha) - \theta_\Lambda(\alpha)}{\theta_L(k^2\alpha) - \theta_\Lambda(k^2\alpha)} &= \frac{\sum_{p \in \Lambda \setminus \{0\}} \pi\alpha |p|^2 (\pi\alpha |p|^2 - 2) e^{-\pi\alpha |p|^2}}{\sum_{p \in \Lambda \setminus \{0\}} \pi\alpha k^2 |p|^2 (\pi\alpha k^2 |p|^2 - 2) e^{-\pi\alpha k^2 |p|^2}} \\ &= k^{-2} \frac{\sum_{p \in \Lambda \setminus \{0\}} \pi\alpha |p|^4 e^{-\pi\alpha |p|^2} - 2 \sum_{p \in \Lambda \setminus \{0\}} |p|^2 e^{-\pi\alpha |p|^2}}{\sum_{p \in \Lambda \setminus \{0\}} \pi\alpha k^2 |p|^4 e^{-\pi\alpha k^2 |p|^2} - 2 \sum_{p \in \Lambda \setminus \{0\}} |p|^2 e^{-\pi\alpha k^2 |p|^2}}. \end{aligned}$$

By absolute convergence, the first term of both numerator and denominator are vanishing as $\alpha \rightarrow 0$. We therefore obtain that

$$\lim_{\alpha \rightarrow 0} \lim_{\substack{L \rightarrow \Lambda \\ L \neq \Lambda}} \frac{\theta_L(\alpha) - \theta_\Lambda(\alpha)}{\theta_L(k^2\alpha) - \theta_\Lambda(k^2\alpha)} = \lim_{\alpha \rightarrow 0} k^{-2} \frac{\sum_{p \in \Lambda \setminus \{0\}} |p|^2 e^{-\pi\alpha |p|^2}}{\sum_{p \in \Lambda \setminus \{0\}} |p|^2 e^{-\pi\alpha k^2 |p|^2}} = 0,$$

by comparing the convergence rate of these two exponential sums that are going to $+\infty$ as $\alpha \rightarrow 0$. It follows that (4.1) does not hold for $\alpha < \alpha_d$ where α_d depends on d, k and a_k , and the proof of the first part of the theorem is completed.

The second part of the theorem is a simple consequence of the fact that f_κ defined by (1.8) belongs to \mathcal{F}_d^{cm} if $f \in \mathcal{F}_d^{cm}$ and $a_k < 0$ for all $k \in K$. \square

The proof of our second result, namely Theorem 2.4, is a direct and simple consequence of our work [9].

Proof of Theorem 2.4. If $p_{i,k}/k = c_L$ modulo L for all $k \in K$ and all $i \in I_k$, we obtain

$$\begin{aligned} E_f^\kappa[L] &= E_f[L] - \sum_{k \in K} a_k \sum_{i \in I_k} \sum_{p \in L} f \left(k^2 \left| \frac{p_{i,k}}{k} + p \right|^2 \right) \\ &= E_f[L] - \sum_{k \in K} a_k \#L_k E_{f(k^2 \cdot)}[L + c_L]. \end{aligned}$$

As proved in [9], for any $f \in \mathcal{F}_2^{cm}$, A_2 is the unique maximizer of $L \mapsto E_f[L + c_L]$ in $\mathcal{L}_2(1)$. It follows that A_2 , which uniquely minimizes E_f in $\mathcal{L}_2(1)$ is the unique minimizer of E_f^κ in $\mathcal{L}_2(1)$ since $a_k > 0$ for all $k \in K$. \square

We now show Theorem 2.9 which gives a simple criterion for the conservation of the minimality of a universal optimizer.

Proof of Theorem 2.9. In order to show the three first points, it is sufficient to show the first point of our theorem, i.e., the fact that $d\mu_{f_\kappa}(t) = (\rho_f(t) - \sum_{k \in K} a_k k^{-2} \rho_f(\frac{t}{k^2})) dt$. We remark that ρ_f is the inverse Laplace transform of f , i.e., $\rho_f(t) = \mathcal{L}^{-1}[f](t)$. By linearity, it follows that

$$d\mu_{f_\kappa}(t) = \rho_{f_\kappa}(t) dt, \quad \text{where} \quad \rho_{f_\kappa}(t) = \rho_f(t) - \sum_{k \in K} a_k \mathcal{L}^{-1}[f(k^2 \cdot)](t).$$

By the basic properties of the inverse Laplace transform, we obtain that, for all $t > 0$,

$$\mathcal{L}^{-1}[f(k^2 \cdot)](t) = k^{-2} \mathcal{L}^{-1}[f](k^{-2}t) = k^{-2} \rho_f(k^{-2}t),$$

and our result follows by the universal optimality of L_d in $\mathcal{L}_d(1)$ and the definition of completely monotone function.

To show the last point of our theorem, we adapt [4, Thm. 1.1]. Let $L \in \mathcal{L}_d(1)$ and $V > 0$, then we have

$$\begin{aligned} E_f^\kappa[V^{\frac{1}{d}}L] &= \sum_{p \in L \setminus \{0\}} f_\kappa(V^{\frac{2}{d}}|p|^2) = \int_0^\infty \left[\theta_L\left(\frac{V^{\frac{2}{d}}t}{\pi}\right) - 1 \right] \rho_{f_\kappa}(t) dt \\ &= \frac{\pi}{V^{\frac{2}{d}}} \int_0^\infty [\theta_L(y) - 1] \rho_{f_\kappa}\left(\frac{\pi y}{V^{\frac{2}{d}}}\right) dy \\ &= \frac{\pi}{V^{\frac{2}{d}}} \int_0^1 [\theta_L(y) - 1] \rho_{f_\kappa}\left(\frac{\pi y}{V^{\frac{2}{d}}}\right) dy + \frac{\pi}{V^{\frac{2}{d}}} \int_1^\infty [\theta_L(y) - 1] \rho_{f_\kappa}\left(\frac{\pi y}{V^{\frac{2}{d}}}\right) dy \\ &= \frac{\pi}{V^{\frac{2}{d}}} \int_1^\infty \left[\theta_L\left(\frac{1}{y}\right) - 1 \right] \rho_{f_\kappa}\left(\frac{\pi}{yV^{\frac{2}{d}}}\right) y^{-2} dy \\ &\quad + \frac{\pi}{V^{\frac{2}{d}}} \int_1^\infty [\theta_L(y) - 1] \rho_{f_\kappa}\left(\frac{\pi y}{V^{\frac{2}{d}}}\right) dy. \end{aligned} \tag{4.2}$$

A simple consequence of the Poisson summation formula is the well-known identity (see, e.g., [25, Eq. (43)])

$$\forall y > 0, \quad \theta_L\left(\frac{1}{y}\right) = y^{\frac{d}{2}} \theta_{L^*}(y). \tag{4.3}$$

From (4.3), we see that if L_d is the unique minimizer of $L \mapsto \theta_L(\alpha)$ for all $\alpha > 0, L \in \mathcal{L}_d(1)$ then $L_d^* = L_d$. From (4.2) and (4.3), for all $V > 0, L \in \mathcal{L}_d(1)$, we have

$$\begin{aligned} E_f^\kappa[V^{\frac{1}{d}}L] &= \frac{\pi}{V^{\frac{2}{d}}} \int_1^\infty \left[y^{\frac{d}{2}} \theta_{L^*}(y) - 1 \right] \rho_{f_\kappa}\left(\frac{\pi}{yV^{\frac{2}{d}}}\right) y^{-2} dy \\ &\quad + \frac{\pi}{V^{\frac{2}{d}}} \int_1^\infty [\theta_L(y) - 1] \rho_{f_\kappa}\left(\frac{\pi y}{V^{\frac{2}{d}}}\right) dy. \end{aligned} \tag{4.4}$$

and

$$\begin{aligned} E_f^\kappa[V^{\frac{1}{d}}L] - E_f^\kappa[V^{\frac{1}{d}}L_d] &= \frac{\pi}{V^{\frac{2}{d}}} \int_1^\infty [\theta_{L^*}(y) - \theta_{L_d}(y)] \rho_{f_\kappa}\left(\frac{\pi}{yV^{\frac{2}{d}}}\right) y^{\frac{d}{2}-2} dy \\ &\quad + \frac{\pi}{V^{\frac{2}{d}}} \int_1^\infty [\theta_L(y) - \theta_{L_d}(y)] \rho_{f_\kappa}\left(\frac{\pi y}{V^{\frac{2}{d}}}\right) dy. \end{aligned} \tag{4.5}$$

By (4.5) and the definition of g_V , if V is such that $g_V(y) \geq 0$ for a.e. $y \geq 1$ then

$$\begin{aligned} E_f^\kappa[V^{\frac{1}{d}}L] - E_f^\kappa[V^{\frac{1}{d}}L_d] &+ E_f^\kappa[V^{\frac{1}{d}}L^*] - E_f^\kappa[V^{\frac{1}{d}}L_d] \\ &= \frac{\pi}{V^{\frac{2}{d}}} \int_1^\infty [\theta_{L^*}(y) - \theta_{L_d}(y)] g_V(y) dy + \frac{\pi}{V^{\frac{2}{d}}} \int_1^\infty [\theta_L(y) - \theta_{L_d}(y)] g_V(y) dy \\ &\geq \frac{\pi}{V^{\frac{2}{d}}} \int_1^\infty m_L(y) g_V(y) dy, \end{aligned} \tag{4.6}$$

where

$$m_L(y) := \min\{\theta_{L^*}(y) - \theta_{L_d}(y), \theta_L(y) - \theta_{L_d}(y)\}.$$

Since $m_L(y) \geq 0$ for all $L \in \mathcal{L}_d(1), y > 0$ with equality if and only if $L = L_d$, and $g_V(y) \geq 0$ for a.e. $y \in [1, \infty)$, we get from (4.6) that

$$E_f^\kappa[V^{\frac{1}{d}}L] + E_f^\kappa[V^{\frac{1}{d}}L^*] \geq 2E_f^\kappa[V^{\frac{1}{d}}L_d], \quad \text{with equality if and only if } L = L_d.$$

It follows that L_d is the unique minimizer of $L \mapsto E_f^\kappa[V^{\frac{1}{d}}L]$ on $\mathcal{L}_d(1)$, or equivalently that $V^{\frac{1}{d}}L_d$ is the unique minimizer of E_f^κ in $\mathcal{L}_d(V)$, and the result is proved. \square

The previous proof contains the main ingredients for showing Theorem 2.11.

Proof of Theorem 2.11. Following exactly the same sequence of arguments as in the proof of the fourth point of Theorem 2.9, we obtain the maximality result of $V^{\frac{1}{d}}L_d^\pm$ at fixed density for E_f^\pm . Indeed, (4.3) is replaced by

$$\theta_L^\pm(\alpha) = y^{\frac{d}{2}}\theta_{L^*+c_{L^*}}(\alpha),$$

and, by using the maximality of L_d^\pm for $L \mapsto \theta_L^\pm(\alpha)$ and $L \mapsto \theta_{L+c_L}(\alpha)$ for all $\alpha > 0$, we obtain

$$\begin{aligned} & E_f^\pm[V^{\frac{1}{d}}L] - E_f^\pm[V^{\frac{1}{d}}L_d] + E_f^\pm[V^{\frac{1}{d}}L^*] - E_f^\pm[V^{\frac{1}{d}}L_d] \\ &= \frac{\pi}{V^{\frac{2}{d}}} \int_1^\infty \left[\theta_{L^*+c_{L^*}}(y) - \theta_{L_d^\pm+c_{L_d^\pm}}(y) \right] g_V(y) dy \\ & \quad + \frac{\pi}{V^{\frac{2}{d}}} \int_1^\infty \left[\theta_L^\pm(y) - \theta_{L_d^\pm}^\pm(y) \right] g_V(y) dy \\ & \leq \frac{\pi}{V^{\frac{2}{d}}} \int_1^\infty m_L^\pm(y) g_V(y) dy, \end{aligned} \tag{4.7}$$

where

$$m_L^\pm(y) := \max\{\theta_{L^*+c_{L^*}}(y) - \theta_{L_d^\pm+c_{L_d^\pm}}(y), \theta_L^\pm(y) - \theta_{L_d^\pm}^\pm(y)\}.$$

We again remark that $m_L^\pm(y) \leq 0$ for all $L \in \mathcal{L}_d(1), y > 0$ with equality if and only if $L = L_d^\pm$. Therefore, the positivity of g_V as well as the universal maximality of L_d^\pm implies in the same way that $V^{\frac{1}{d}}L_d^\pm$ is the unique maximizer of E_f^\pm in $\mathcal{L}_d(V)$. \square

The proof of Corollary 2.13 is a straightforward consequence of Theorem 2.9.

Proof of Corollary 2.13. Let $A_K := \{a_k\}_{k \in K} \subset \mathbb{R}_+$ be such that $\mathbf{L}(A_K, 2) \leq 1$. Since $\mu_f \geq 0$, it follows that ρ_f is positive, and furthermore ρ_f is increasing by assumption. Therefore, we have, for all $t > 0$,

$$\sum_{k \in K} \frac{a_k}{k^2} \rho_f\left(\frac{t}{\alpha^2}\right) \leq \sum_{k \in K} \frac{a_k}{k^2} \rho_f(t) = \mathbf{L}(A_K, 2) \rho_f(t) \leq \rho_f(t),$$

where the first inequality is obtained from the monotonicity of ρ_f and the last one from its positivity and the fact that $L(A_K, 2) \leq 1$. The proof is completed by applying Theorem 2.9. \square

We now show Theorem 2.15 which is a simple consequence of the homogeneity of the Epstein zeta function and a property of the Riemann zeta function.

Proof of Theorem 2.15. Using the homogeneity of the Epstein zeta function, we obtain

$$E_f^\kappa[L] = \sum_{p \in L \setminus \{0\}} \frac{1}{|p|^{2s}} - \sum_{k \in K} \sum_{p \in L \setminus \{0\}} \frac{a_k}{k^{2s}|p|^{2s}} = (1 - L(A_K, 2s)) \zeta_L(2s),$$

the exchange of sums being ensured by their absolute summability. If $L(A_K, 2s) < 1$, then $L \mapsto \zeta_L(2s)$ and E_f^κ have exactly the same minimizer. If $L(A_K, 2s) > 1$, then the optimality are reversed and the proof is complete.

Furthermore, if $a_k = 1$ for all $k \in K$, then we have

$$L(A_K, 2s) = \sum_{k \in K} \frac{1}{k^{2s}} \leq \zeta(2s) - 1,$$

where $\zeta(s) := \sum_{n \in \mathbb{N}} n^{-s}$ is the Riemann zeta function. Since $\zeta(x) < 2$ on $(0, \infty)$ if and only if $x > x_0 \approx 1.73$, it follows that $\zeta(2s) - 1 < 1$ if and only if $s > x_0/2 \approx 0.865$ which is true for all $s > d/2$ whenever $d \geq 2$. We thus have $L(A_K, 2s) < 1$ and the proof is completed by application of point 1. of the theorem. \square

Before proving Theorem 2.17, we derive the following result, a generalization of our two-dimensional theorem [4, Prop. 6.11]. Its proof follows the same main arguments as the two-dimensional version and it is a consequence of point 4. of Theorem 2.9.

Proposition 4.1. (Optimality at high density for Lennard-Jones-type potentials) *Let $f(r) = \frac{b_2}{r^{x_2}} - \frac{b_1}{r^{x_1}}$ where $b_1, b_2 \in (0, \infty)$ and $x_2 > x_1 > d/2$, and let L_d be universally optimal in $\mathcal{L}_d(1)$. If*

$$V \leq \pi^{\frac{d}{2}} \left(\frac{b_2 \Gamma(x_1)}{b_1 \Gamma(x_2)} \right)^{\frac{d}{2(x_2 - x_1)}},$$

then $V^{\frac{1}{d}} L_d$ is the unique minimizer of E_f in $\mathcal{L}_d(V)$.

Proof of Proposition 4.1. We follow the lines of [4, Prop. 6.10] and we apply point 4. of Theorem 2.9. For $i \in \{1, 2\}$, let $\beta_i := b_i \frac{\pi^{x_i-1}}{\Gamma(x_i)}$ and $\alpha := V^{\frac{2}{d}}$, then $g_V(y) = \frac{y^{\frac{d}{2} - x_2 - 1}}{\alpha^{x_1 - 1}} \tilde{g}_V(y)$ where g_V is given by (2.3) and

$$\tilde{g}_V(y) := \frac{\beta_2}{\alpha^{x_2 - x_1}} y^{2x_2 - \frac{d}{2}} - \beta_1 y^{x_2 + x_1 - \frac{d}{2}} - \beta_1 y^{x_2 - x_1} + \frac{\beta_2}{\alpha^{x_2 - x_1}}.$$

We therefore compute $\tilde{g}'_V(y) = y^{x_2 - x_1 - 1} u_V(y)$ where

$$u_V(y) := \beta_2 \left(2x_2 - \frac{d}{2} \right) \frac{y^{x_2 + x_1 - \frac{d}{2}}}{\alpha^{x_2 - x_1}} - \beta_1 \left(x_2 + x_1 - \frac{d}{2} \right) y^{2x_1 - \frac{d}{2}} - \beta_1 (x_2 - x_1).$$

Differentiating again, we obtain

$$u'_V(y) = \left(x_2 + x_1 - \frac{d}{2}\right) y^{2x_1 - \frac{d}{2} - 1} \left(\beta_2 \left(2x_2 - \frac{d}{2}\right) \frac{y^{x_2 - x_1}}{\alpha^{x_2 - x_1}} - \beta_1 \left(2x_1 - \frac{d}{2}\right)\right),$$

and we have that $u'_V(y) \geq 0$ if and only if $y \geq \left(\frac{\beta_1(2x_1 - \frac{d}{2})}{\beta_2(2x_2 - \frac{d}{2})}\right)^{\frac{1}{x_2 - x_1}} \alpha$. By assumption, we know that

$$\alpha \leq \pi \left(\frac{a_2 \Gamma(x_1)}{a_1 \Gamma(x_2)}\right)^{\frac{1}{x_2 - x_1}} = \left(\frac{\beta_2}{\beta_1}\right)^{\frac{1}{x_2 - x_1}} < \left(\frac{\beta_2(2x_2 - \frac{d}{2})}{\beta_1(2x_1 - \frac{d}{2})}\right)^{\frac{1}{x_2 - x_1}},$$

which implies that $u'_V(y) \geq 0$ for all $y \geq 1$. We now remark that

$$u_V(1) = \left(2x_2 - \frac{d}{2}\right) \left(\frac{\beta_2}{\alpha^{x_2 - x_1}} - \beta_1\right) \geq 0,$$

by assumption, since $p > d/2 > d/4$ and

$$\alpha \leq \pi \left(\frac{b_2 \Gamma(x_1)}{b_1 \Gamma(x_2)}\right)^{\frac{1}{x_2 - x_1}} \iff \frac{\beta_2}{\alpha^{x_2 - x_1}} - \beta_1 \geq 0. \tag{4.8}$$

It follows that $g'_V(y) \geq 0$ for all $y \geq 1$. Since

$$g_V(1) = 2 \left(\frac{\beta_2}{\alpha^{x_2 - 1}} - \frac{\beta_1}{\alpha^{x_1 - 1}}\right) \geq 0$$

again by (4.8), $g_V(y) \geq 0$ for all $y \geq 1$ and the proof is complete. □

Proof of Theorem 2.17. Let $A_K = \{a_k\}_{k \in K}$ for some $K \subset \mathbb{N} \setminus \{1\}$ and $f(r) = c_2 r^{-x_2} - c_1 r^{-x_1}$, then we have, using the homogeneity of the Epstein zeta function,

$$\begin{aligned} E_f^\kappa[L] &= c_2 \zeta_L(2x_2) - c_1 \zeta_L(2x_1) - \sum_{k \in K} a_k (c_2 \zeta_{kL}(2x_2) - c_1 \zeta_{kL}(2x_1)) \\ &= c_2 (1 - L(A_K, 2x_2)) \zeta_L(2x_2) - c_1 (1 - L(A_K, 2x_1)) \zeta_L(2x_1). \end{aligned}$$

We now assume that $L(A_K, 2x_2) < L(A_K, 2x_1) < 1$. Therefore, the first part of point 1. is a simple consequence of Proposition 4.1 applied for the coefficients $b_i = c_i (1 - L(A_K, 2x_i)) > 0$ where $i \in \{1, 2\}$. The fact that E_f^κ is not minimized by L_d for V large enough is a direct application of [14, Thm. 1.5(1)] since μ_f is negative on $(0, r_0)$ for some r_0 depending on the parameters c_1, c_2, x_1, x_2, A_K . Furthermore, the fact that the shape of the minimizers are the same follows from [14, Thm. 1.11] where it is shown that the minimizer of the Lennard-Jones-type lattice energies does not depend on the coefficients b_1, b_2 but only on the exponents x_1, x_2 , which are the same for f and f_κ .

If $L(A_K, 2x_1) > L(A_K, 2x_2) > 1$, then $f_\kappa(r) = -b_2 r^{-x_2} + b_1 r^{-x_1}$ where $b_i := c_i (L(A_K, 2x_i) - 1) > 0, i \in \{1, 2\}$. It follows that $f_\kappa(r)$ tends to $-\infty$ as $r \rightarrow 0$, which implies the same for $E_f^\kappa[L]$ as L has its lengths going to 0 and $+\infty$, i.e., when L collapses. This means that E_f^κ does not have a minimizer in $\mathcal{L}_d(V)$ and in \mathcal{L}_d . Furthermore, combining point 1. with the fact that the

signs of the coefficients are switched, we obtain the maximality of $V^{1/d}L_d$ at high density (i.e., low volume $V < V_\kappa$).

If $L(A_K, 2x_1) > 1 > L(A_K, 2x_2)$, then $f_\kappa(r) = b_2r^{-x_2} + b_1r^{-x_1}$ where $b_1 := c_1(L(A_K, 2x_1) - 1) > 0$ and $b_2 := c_2(1 - L(A_K, 2x_2)) > 0$. Therefore, $f_\kappa \in \mathcal{F}_d^{cm}$, which implies the optimality of $V^{1/d}L_d$ in $\mathcal{L}_d(V)$ for all fixed $V > 0$ and the fact that $E_f^\kappa[L]$ tends to 0 as all the points are sent to infinity, i.e., E_f^κ does not have a minimizer in \mathcal{L}_d . \square

Acknowledgements

I am grateful for the support of the WWTF research project ‘Variational Modeling of Carbon Nanostructures’ (No. MA14-009) and the (partial) financial support from the Austrian Science Fund (FWF) Project F65. I also thank Mircea Petrache for our discussions about the crystallization at fixed density as a consequence of Cohn–Kumar conjecture stated in Remark 2.10. I also thank the anonymous referees for their useful suggestions and comments.

Funding Open access funding provided by University of Vienna.

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Communicated by Christian Maes.

Received: August 3, 2020.

Accepted: March 10, 2021.