FINITE CRYSTALLIZATION AND WULFF SHAPE EMERGENCE FOR IONIC COMPOUNDS IN THE SQUARE LATTICE

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Abstract. We present two-dimensional crystallization results in the square lattice for finite particle systems consisting of two different atomic types. We identify energy minimizers of configurational energies featuring two-body short-ranged particle interactions which favor some reference distance between different atomic types and contain repulsive contributions for atoms of the same type. We first prove that ground states are connected subsets of the square lattice with alternating arrangement of the two atomic types in the crystal lattice, and address the emergence of a square macroscopic Wulff shape for an increasing number of particles. We then analyze the signed difference of the number of the two atomic types, the so-called net charge, for which we prove the sharp scaling $\mathrm{O}(n^{1/4})$ in terms of the particle number n. Afterwards, we investigate the model under prescribed net charge. We provide a characterization for the minimal energy and identify a critical net charge beyond which crystallization in the square lattice fails. Finally, for this specific net charge we prove a crystallization result and identify a diamond-like Wulff-shape of energy minimizers which illustrates the sensitivity of the macroscopic geometry on the net charge.

1. Introduction

The question whether the ground states of particle systems for certain configurational energies arrange themselves into crystalline order is referred to as the crystallization problem [5]. Due to its paramount theoretical and applicative relevance, this mathematical issue has attracted a great deal of attention over the last decades and has led to various mathematically rigorous crystallization results for ensembles consisting of *one single* atomic type. For particle systems with different types of atoms, however, rigorous results appear to be scarce. The goal of this paper is to contribute to these fundamental mathematical questions by presenting a study of crystallization in the two-dimensional square lattice for finite particle systems consisting of *two different* atomic types.

Microscopically, crystallization can be seen as the result of interatomic interactions governed by quantum mechanics. At zero or very low temperature, atomic interactions are expected to depend only on the geometry of the atomic arrangement. In this case, configurations can be identified with the respective positions of identical atoms $\{x_1, \dots, x_n\}$. Then the crystallization problem consists in considering the minimization of a configurational energy $\mathcal{E}(\{x_1, \dots, x_n\})$ and in proving or disproving the periodicity of ground-state configurations of $\mathcal{E}$.

Various such crystallization results for different choices of the energy $\mathcal{E}$ comprising classical interaction potentials have been derived over the last decades. Here, among the vast body of literature, we only mention some of the relevant works, and refer the reader to the recent review [5] for a general perspective. Concerning results in one dimension we mention [18, 19, 28, 33], and we refer to [10, 20, 23, 25, 27, 34] for studies in dimension two for a finite number of identical particles. In particular, we highlight the work by Mainini, Piovano, and Stefanelli [23] where a comprehensive analysis of crystallization in the square lattice is performed. Besides crystallization, the authors also provide a fine characterization of ground-state geometries by proving the emergence of a square macroscopic Wulff shape for growing particle numbers. (We also refer to [2, 8, 9, 24] for similar studies for different lattices.) Under less restrictive assumptions on the potentials, various results have been obtained in the thermodynamic limit [11, 12, 32],

2010 *Mathematics Subject Classification.* 82D25.

Key words and phrases. Ionic dimers, ground state, configurational energy minimization, crystallization, Wulff shape, square lattice, net charge.

i.e., as the number of particles tends to infinity. The crystallization problem in three dimension seems to be very difficult and only few rigorous results [14, 15, 21, 31] are available.

For particle systems involving different types of atoms, simulations are abundant, but rigorous results seem to be limited to [3, 6, 16, 29]. To the best of our knowledge, the recent work [16] by the authors represents a first rigorous mathematical crystallization result for two-dimensional *dimers*, i.e., molecular compounds consisting of two atomic types. This result is inspired by problems for systems of identical particles and follows the classical molecular-mechanical frame of configurational energy minimization: configurations of n particles are identified with their respective *positions* $\{x_1, \dots, x_n\} \subset \mathbb{R}^2$ and additionally with their *types* $\{q_1, \dots, q_n\} \in \{-1, 1\}^n$. The goal is to determine minimizers of a corresponding interaction energy $\mathcal{E}(\{(x_1, q_1), \dots, (x_n, q_n)\})$ and to characterize their geometry.

More precisely, the energy $\mathcal{E} = \mathcal{E}_{\rm a} + \mathcal{E}_{\rm r}$ is assumed to consist of two short-ranged two-body interaction potentials $\mathcal{E}_{\rm a}$ and $\mathcal{E}_{\rm r}$, where $\mathcal{E}_{\rm a}$ represents the interactions between atoms of different type and $\mathcal{E}_{\rm r}$ encodes the energy contributions of atoms having the same type. The potential $\mathcal{E}_{\rm a}$ is attractive-repulsive and favors atoms sitting at some specific reference distance, whereas $\mathcal{E}_{\rm r}$ is a pure repulsive term. The main result of [16] is that, for specific quantitative assumptions on the potentials, global minimizers of the configurational energy are essentially connected subsets of the regular hexagonal lattice with the two atomic types alternating. The first main goal of the present article is to show that weaker short-ranged repulsive terms favor crystallization in the square lattice, which illustrates the sensitivity of the ground-state geometry on the precise assumptions on the potentials.

Let us mention that the choice of the interaction potentials is motivated by the modeling of ions in ionic compounds. In fact, one can interpret the two interaction energies as (simplified) Coulomb-interactions between ions of equal and opposite charge. We will therefore often refer to the atomic types $\{q_1, \dots, q_n\} \in \{-1, 1\}^n$ as positive or negative *charges*. In this context, it is interesting to consider the *net charge* $\sum_{i=1}^n q_i$, i.e., the (signed) difference of the number of the two atomic types.

In [16], the *free net charge problem* has been addressed, i.e., the net charge is not preassigned but a fundamental part of the minimization problem. It has been shown that $\sum_{i=1}^n q_i$ is 'almost neutral', with a deviation from zero of order $\mathrm{O}(n^{1/4})$, where the scaling in terms of the particle number n is sharp. Similar problems of charge distributions and net charge on Bravais lattices have been recently studied in [4]. Besides extending the results of the free net charge problem to the present setting, the second main goal of this article is to complement the aforementioned analysis by studying the *prescribed net charge problem*, i.e., the net charge is a given constraint in the minimization problem. This corresponds to a model of a closed physical system containing a certain number of positively and negatively charged atoms.

We now give an overview of the main results of this article representing a comprehensive analysis of finite crystallization for dimers in the two-dimensional square lattice, see Section 2.3 for details.

(1) We first address the free net charge problem. Under suitable assumptions on the attractive and the repulsive potentials, we characterize the ground-state energy and geometry of finite particle configurations of ions in dimension two. In particular, we prove that each global minimizer of the configurational energy is essentially a connected subset of the square lattice with alternating arrangement of the two atomic types in the crystal lattice. This characterization holds except for possibly one atom at the boundary of the configuration. Similar to [23], we identify the emergence of a square macroscopic Wulff shape for growing particle numbers.
(2) We provide a fine asymptotic characterization for the net charge as the number of atoms n grows. More specifically, we show that the fluctuation of the net charge around zero can be at most of order $\mathrm{O}(n^{1/4})$, i.e., $|\sum_{i=1}^n q_i| \le cn^{1/4}$ for some constant $c > 0$ independent of n. By providing an explicit construction we further prove that this scaling is sharp.
(3) We consider the prescribed net charge problem and provide a characterization of the minimal energy in dependence of the net charge. We identify a critical net charge, the so-called *saturation net charge* $q_{\rm sat}$, which corresponds to the case that all atoms of the less frequent atomic type are bonded to exactly four other atoms. By way of example, see Fig. 5, we show that $q_{\rm sat}$ is critical

in the sense that beyond this specific net charge we cannot expect that atoms arrange themselves in a regular lattice.

(4) We investigate the geometry of energy minimzers for prescribed net charge $q_{\rm sat}$ and show that also in this case optimal configurations are (essentially) subsets of the square lattice. Our interest in this specific case is twofold: (i) this problem together with the free net charge problem (which by (2) essentially corresponds to the problem with prescribed net charge zero) constitute the extreme cases for which crystallization results can be shown. (ii) for $q_{\rm sat}$, we identify a macroscopic diamond-like Wulff-shape, which illustrates the dependence of the macroscopic geometry on the prescribed net charge.

Our general proof strategy for the free net charge problem follows the induction method on bond-graph layers developed in [20, 23, 25, 27]. Let us mention that our problem is particularly related to [23], where crystallization for identical particles in the square lattice has been investigated under three-body angular potentials. Actually, the ground-state energy in the present context coincides with the one obtained there. A crucial point in the induction step is the derivation of a boundary energy estimate. The presence of repulsive instead of angular terms calls for a novel definition of the boundary energy, complementing the approach in [23] from a technical point of view, see Remark 5.2.

To prove the emergence of a square Wulff shape and the sharp scaling $\mathrm{O}(n^{1/4})$ for the net charge, we use the fact that in ground states the two atomic types are alternately arranged in the square lattice. This allows us to apply the $n^{3/4}$-law in [23] which states that ground states differ from a square shape by at most $\mathrm{O}(n^{3/4})$ atoms, or equivalently, by at most $\mathrm{O}(n^{1/4})$ in Hausdorff distance.

Concerning the proof of the results for the prescribed net charge problem, in principle we follow the same induction method on bond-graph layers as for the free net charge problem. The actual realization, however, is much more delicate. In fact, as a preliminary step for a crystallization result in the square lattice, a fine characterization of the saturation net charge $q_{\rm sat}$ is needed. Then it turns out that the geometry of optimal configurations under prescribed net charge $q_{\rm sat}$ is quite flexible: by way of explicit constructions (see, e.g., Fig. 6 and Fig. 9), we observe that optimal configurations are possibly not connected or regions at the boundary are not contained in the square lattice. Fine geometric arguments are necessary to ensure that these degenerate parts consist of a controlled number of atoms only. For the identification of the global diamond-like Wulff-shape, we identify the charge of configurations with the ∞-perimeter of specific interpolations, and then, following an idea inspired by [7], we apply the quantitative isoperimetric inequality to obtain a bound on the deviations from a diamond.

The article is organized as follows. In Section 2 we introduce the precise mathematical setting and present the main results about the free and prescribed net charge problem. In Section 3 we construct explicitly some configurations in order to provide sharp upper bounds for the ground-state energy and the net charge. Moreover, we establish an upper bound for the saturation net charge $q_{\rm sat}$. These explicit constructions already give the right intuition for the microscopic and macroscopic geometry of optimal configurations. In Section 4 we discuss elementary geometric properties of energy minimizers. In Section 5 we give the lower bound for the ground-state energy and provide a fine characterization of the geometry of ground states. Here, we also prove the $n^{1/4}$-law for the net charge of ground states. Finally, Section 6 is devoted to the prescribed net charge problem. We first provide a lower bound for $q_{\rm sat}$ matching the upper bound derived in Section 3. Afterwards, we characterize the geometry of $q_{\rm sat}$-optimal configurations.

2. Setting and main results

In this section we first introduce our model and give some basic definitions. Afterwards, we present our main results.

2.1. Configurations and interaction energy.

We consider particle systems in two dimensions consisting of two different atomic types. We model their interaction by classical potentials in the frame of Molecular Mechanics [1, 17, 22]. Let $n \in \mathbb{N}$. We indicate the *configuration* of n particles by

$$C_n = \{(x_1, q_1), \dots, (x_n, q_n)\} \subset \left(\mathbb{R}^2 \times \{-1, 1\}\right)^n,$$

identified with the respective *atomic positions* $X_n = (x_1, \dots, x_n) \in \mathbb{R}^{2n}$ together with their types $Q_n = (q_1, \dots, q_n) \in \{-1, 1\}^n$. By referring to a model for ionic dimers, we will often call Q_n the *charges* of the atoms, $q = 1$ representing *cations* and $q = -1$ representing *anions*. Our choice of the empirical potentials (see below) is indeed inspired by ions in ionic compounds, which are primarily held together by their electrostatic forces between the net negative charge of the anions and the net positive charge of the cations [26].

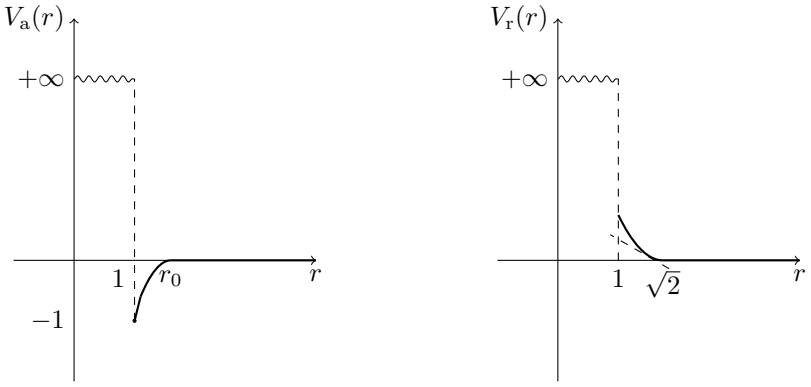

FIGURE 1. The potentials $V_{\rm a}$ and $V_{\rm r}$.

By following the setting in [16], we define the energy $\mathcal{E} : (\mathbb{R}^2 \times \{-1, 1\})^n \to \overline{\mathbb{R}}$ of a given configuration $\{(x_1, q_1), \dots, (x_n, q_n)\} \in (\mathbb{R}^2 \times \{-1, 1\})^n$ by

$$\mathcal{E}(C_n) = \frac{1}{2} \sum_{\substack{i \neq j \\ q_i = q_j}} V_{\rm r}(|x_i - x_j|) + \frac{1}{2} \sum_{\substack{i \neq j \\ q_i \neq q_j}} V_{\rm a}(|x_i - x_j|), \tag{2.1}$$

where $V_{\rm r}, V_{\rm a} : [0, +\infty) \to \overline{\mathbb{R}}$ are a *repulsive potential* and an *attractive-repulsive potential*, respectively. The factor $1/2$ accounts for the fact that every contribution is counted twice in the sum. The two potentials are pictured schematically in Fig. 1. Let $r_0 \in [1, (2\sin(\frac{\pi}{7}))^{-1})$ and note that $r_0 < \sqrt{2}$. The attractive-repulsive potential $V_{\rm a}$ satisfies

[i] $V_{\rm a}(r) = +\infty$ for all $r < 1$,

[ii] $V_{\rm a}(r) = -1$ if and only if $r = 1$ and $V_{\rm a}(r) > -1$ otherwise,

[iii] $V_{\rm a}(r) \leq 0$ for all $r \geq 1$ with equality for all $r > r_0$.

The distance $r = 1$ represents the (unique) equilibrium distance of two atoms with opposite charge. The choice of $V_{\rm a}$ reflects a balance between a long-ranged Coulomb attraction and the short-ranged Pauli repulsion acting when a pair of ions comes too close to each other. Assumption [iii] restricts the interaction range and guarantees that the *bond graph* is planar, see Section 2.2.

The repulsive potential $V_{\rm r}$ satisfies

[iv] $V_{\rm r}(r) = +\infty$ for all $r < 1$ and $0 \leq V_{\rm r}(r) < +\infty$ for all $r \geq 1$,

[v] $V_{\rm r}$ is non-increasing and convex for $r \geq 1$,

[vi] $V_{\rm r}\left(2r_0 \sin\left(\frac{\pi}{5}\right)\right) > 6$,

[vii] $V_{\rm r}(r) = 0$ if and only if $r \geq \sqrt{2}$.

The natural assumption [v] is satisfied for example for repulsive Coulomb interactions. We emphasize that some quantitative requirements of the form [vi] and [vii] are necessary to obtain a crystallization result in the square lattice. Other quantitative assumptions on the repulsive potential will favor, e.g., that the atoms arrange themselves in a hexagonal lattice, see [16].

Finally, we require the following *slope conditions*

[viii] $V'_{\mathrm{r},-}(\sqrt{2}) < -\dfrac{16}{\sqrt{2}\pi}, \qquad \dfrac{1}{r-1}(V_{\mathrm{a}}(r) - V_{\mathrm{a}}(1)) > -\dfrac{1}{2}V'_{\mathrm{r},+}(1) \quad \text{for all } r \in (1, r_0],$

where the functions $V'_{\mathrm{r},-}$, $V'_{\mathrm{r},+}$ denote the left and right derivative, respectively. (They exist due to the convexity of V_{r}.) These conditions are reminiscent of the soft-interaction assumption by Radin [27] and the slope condition for an angular potential by Mainini, Piovano, and Stefanelli [23]. For a more detailed discussion on the assumptions on V_{a} and V_{r} we refer the reader to [16, Section 2.1].

2.2. **Basic notions.** In this subsection we collect some basic notions. Consider a configuration $C_n \in \big(\mathbb{R}^2 \times \{-1,1\}\big)^n$ with finite energy consisting of the positions $X_n = (x_1, \dots, x_n) \in \mathbb{R}^{2n}$ and the charges $Q_n = (q_1, \dots, q_n) \in \{-1,1\}^n$.

Neighborhood, bonds, angles: For each $x_i \in \mathbb{R}^2$, $i \in \{1, \dots, n\}$, we define the *neighborhood* by

$$\mathcal{N}(x_i) = (X_n \setminus \{x_i\}) \cap \{x \in \mathbb{R}^2 : \ |x - x_i| \le r_0\}, \tag{2.2}$$

where r_0 is defined in [iii]. If $x_j \in \mathcal{N}(x_i)$, we say that x_i and x_j are *bonded*. We will say that x_i is k-bonded if $\#\mathcal{N}(x_i) = k$. Given $x_j, x_k \in \mathcal{N}(x_i)$, we define the *bond-angle* between x_j, x_i, x_k as the angle between the two vectors $x_k - x_i$ and $x_j - x_i$. (We choose anti-clockwise orientation for definiteness.) In general, we say that it is an angle at x_i.

Bond graph: The set of atomic positions $X_n \subset \mathbb{R}^{2n}$ together with the set of bonds $\{\{x_i, x_j\} : x_j \in \mathcal{N}(x_i)\}$ forms a graph which we call the *bond graph*. Since for configurations with finite energy there holds $\mathrm{dist}(x_i, X_n \setminus \{x_i\}) \ge 1$ and $x_j \in \mathcal{N}(x_i)$ only if $|x_i - x_j| \le r_0 < \sqrt{2}$, their bond graph is a planar. Indeed, given a quadrangle with all sides and one diagonal in $[1, r_0]$, the second diagonal is at least $\sqrt{2} > r_0$. If no ambiguity arises, the number of bonds in the bond graph will be denoted by b, i.e.,

$$b = \#\{\{x_i, x_j\} : x_j \in \mathcal{N}(x_i)\}.$$

We say a configuration is *connected* if each two atoms are joinable through a simple path in the bond graph. In a similar fashion, we speak of connected components of a configuration. Any simple cycle of the bond graph is a *polygon*.

Acyclic bonds: A bond is called *acyclic* if it is not contained in any simple cycle of the bond graph. Among acyclic bonds we distinguish between *flags* and *bridges*. We say that an acyclic bond is a bridge if it is contained in some simple path connecting two vertices which are included in two distinct cycles. All other acyclic bonds are called flags, see Fig. 2.

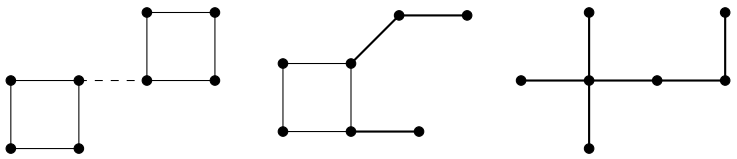

Figure 2. Examples of flags (bold) and a bridge (dashed).

Defects: By elementary polygons we denote polygons which do not contain any non-acyclic bonds in its interior region. An elementary polygon in the bond graph which is not a square is called a *defect*. We introduce the *excess of edges* $\eta(C_n)$ by

$$\eta(C_n) = \sum_{j \ge 4} (j-4) f_j, \tag{2.3}$$

where f_j denotes the number of polygons with j vertices in the bond graph. The excess of edges is a tool to quantify the number of defects in the bond graph. Note that the summation in (2.3) runs over $j \ge 4$. This is due to the fact that we use this definition only for configurations whose bond graph contains only k-gons with $k \ge 4$, cf. Lemma 4.2 below. If it is clear from the context, we omit the dependence on C_n and write $\eta = \eta(C_n)$.

In the following we frequently refer to C_n instead of X_n when speaking about its bond graph, acyclic bonds, or connectedness properties.

Charges: We say that a configuration satisfying

$$\mathcal{N}(x_i) \cap \{x_j \in X_n : q_j = q_i\} = \emptyset \text{ for all } i \in \{1, \dots, n\} \tag{2.4}$$

has *alternating charge distribution*. A configuration is called *repulsion-free* if $|x_i - x_j| \geq \sqrt{2}$ for all $x_i \neq x_j$ with $q_i = q_j$. The *net charge* of a configuration is defined as the (signed) difference of the number of the two atomic types, i.e.,

$$\mathcal{Q}(C_n) := \sum_{i=1}^{n} q_i. \tag{2.5}$$

We note that all possible net charges are given by $\mathcal{Q}_{\rm net}(n) := (2\mathbb{Z} + n \bmod 2) \cap [-n, n]$. If $\mathcal{Q}(C_n) > 0$, we say that the atoms with charge $+1$ represent the *majority phase* and the atoms with charge -1 the *minority phase*. We use a corresponding denomination if $\mathcal{Q}(C_n) < 0$. We denote by

$$X_n^+ := \{x_i \in X_n : q_i = +1\}, \qquad X_n^- := \{x_i \in X_n : q_i = -1\} \tag{2.6}$$

the *positively* and *negatively charged phase*, respectively.

Ground states: For $q_{\rm net} \in \mathcal{Q}_{\rm net}(n)$ we define

$$\mathcal{E}^n_{\rm min}(q_{\rm net}) := \min\left\{\mathcal{E}(C_n) :\, C_n \subset (\mathbb{R}^2 \times \{-1, 1\})^n,\ \mathcal{Q}(C_n) = q_{\rm net}\right\}. \tag{2.7}$$

A configuration C_n with $\mathcal{Q}(C_n) = q_{\rm net}$ and $\mathcal{E}(C_n) = \mathcal{E}^n_{\rm min}(q_{\rm net})$ is called a $q_{\rm net}$*-optimal configuration*. We will often simply call C_n an *optimal configuration*. Moreover, we call C_n a *ground state* if $\mathcal{E}(C_n) = \min_{q_{\rm net} \in \mathcal{Q}_{\rm net}(n)} \mathcal{E}^n_{\rm min}(q_{\rm net})$. In other words, C_n is a ground state if and only if

$$\mathcal{E}(C_n) \leq \mathcal{E}(C_n').$$

for all $C_n' \subset (\mathbb{R}^2 \times \{-1, 1\})^n$.

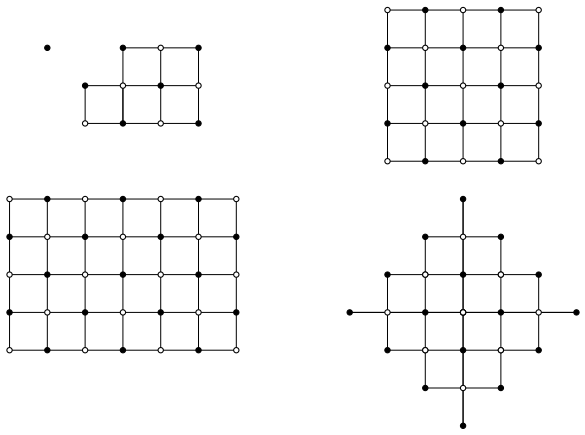

FIGURE 3. Some configurations that are subset of the square lattice. The top configuration on the right is S_n, $25 \leq n \leq 35$, whereas the bottom configuration on the right is D_n, $25 \leq n \leq 40$. The configurations have alternating charge distribution where black indicates $q = +1$ and white indicates $q = -1$.

Subsets of the square lattice: We denote by $\mathbb{Z}^2 \subset \mathbb{R}^2$ the *square lattice*. We define special subsets of the square lattice representing the Wulff-shapes of optimal configurations. For $n \in \mathbb{N}$ we let

$$S_n := \left\{x \in \mathbb{Z}^2 : x_1, x_2 \geq 0,\ |x|_\infty \leq \lfloor \sqrt{n} - 1 \rfloor\right\} \tag{2.8}$$

the *square* of sidelength $\lfloor \sqrt{n} - 1 \rfloor$, where by $\lfloor t \rfloor$ we denote the integer part of $t \in \mathbb{R}$. By

$$D_n := \left\{x \in \mathbb{Z}^2 : |x|_1 \leq \lfloor (-1 + \sqrt{2n - 1})/2 \rfloor\right\} \tag{2.9}$$

we denote the *diamond* of radius $\lfloor(-1+\sqrt{2n-1})/2\rfloor$. S_n and D_n represent the largest squares and diamonds, respectively, with less or equal to n atoms. In Fig. 3 some subsets of the square lattice are depicted.

Observe that these configurations can be chosen to have alternating charge distribution. By assumption [ii],[iii], and [vii] the energy of such configurations C_n satisfies $\mathcal{E}(C_n) = -b$ since all atoms of the same charge have at least distance $\sqrt{2}$ and all atoms of X_n are bonded only to atoms of opposite charge with bonds of unit length.

Equilibrated atoms: We say that an atom $x \in X_n$ is *equilibrated* if all bond-angles at x lie in $\{\frac{\pi}{2}, \pi, \frac{3\pi}{2}\}$. By $\mathcal{A}(X_n)$ we denote the atoms which are *not* equilibrated. Note that, if $\mathcal{A}(X_n) = \emptyset$ and X_n is connected, then X_n is a subset of the square lattice $\mathbb{Z}^2$.

2.3. **Main results.** In this subsection we state our main results. We will first address the free net charge problem, and characterize the energy and geometry of ground states. In particular, we will prove a rigorous planar crystallization result in the spirit of [16, 20, 23, 25, 27] and the emergence of a square macroscopic Wulff shape (cf. [2, 8, 9, 23, 30]). Then we will characterize the net charge of ground-state configurations.

Afterwards, we change the perspective and study q_{net}-optimal configurations under prescribed net charge q_{net}. We give an estimate for the minimal energy $\mathcal{E}^n_{\min}(q_{\text{net}})$ and identify a specific net charge, the *saturation net charge* q^n_{sat}, which corresponds to the smallest net charge where all atoms of the minority phase are 4-bonded. Finally, we prove the emergence of a diamond-like Wulff-shape for q^n_{sat}-optimal configurations which reflects the sensitivity of the Wulff-shape on the prescribed net charge.

Free net charge: Our first result characterizes the energy of ground states. For $n \in \mathbb{N}$, we introduce the function

$$\beta(n) := 2n - 2\sqrt{n}. \tag{2.10}$$

Theorem 2.1 (Ground-state energy)**.** *Let $n \in \mathbb{N}$. Ground states are connected and have alternating charge distribution. They do not contain any bridges. There holds*

$$\mathcal{E}(X_n) = -b = -\lfloor\beta(n)\rfloor. \tag{2.11}$$

Remark 2.2. In view of assumptions [ii] and [vii], we have that $\mathcal{E}(C_n) \geq -b$ with equality if and only if the configuration is repulsion-free and all bonds have unit length. In particular, Theorem 2.1 implies that ground states satisfy both properties.

The next result states that ground states are essentially subsets of the square lattice and that a square Wulff-shape emerges as $n \to \infty$. Without further notice, all following statements regarding the geometry of ground states hold up to isometry. Recall the definition of a square of sidelength $\lfloor\sqrt{n}-1\rfloor$ in (2.8).

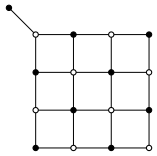

FIGURE 4. A ground state for $n = 17$ that is not a subset of the square lattice.

Theorem 2.3 (Characterization of ground states)**.** *Let $n \in \mathbb{N}$ and let C_n be a ground state.*

(a) *(Crystallization) Except for possibly one atom, C_n is a subset of the square lattice.*
(b) *(Wulff-shape) For a universal constant $c > 0$ independent of n, there holds*

$$\min_{a\in\mathbb{R}^2} \#\big(X_n \triangle (a + S_n)\big) \leq cn^{3/4},$$

where $\triangle$ denotes the symmetric difference of sets.

We point out that, if a ground state contains a flag, it is possibly not a subset of the square lattice, see Fig. 4. Our next result addresses the net charge (2.5) of ground-state configurations.

Theorem 2.4 (Net charge of ground states)**.** *The following properties for the net charge hold:*

(a) *(Net charge control) There exists a universal constant $c > 0$ such that for all $n \in \mathbb{N}$ and all ground states C_n the net charge satisfies $|\mathcal{Q}(C_n)| \leq cn^{1/4}$.*
(b) *(Sharpness of the $n^{1/4}$-scaling) There exists an increasing sequence of integers $(n_j)_j$ and ground states $(C_{n_j})_j$ such that*

$$\liminf_{j\to+\infty} n_j^{-1/4}|\mathcal{Q}(C_{n_j})| > 0.$$

The sharp scaling $n^{1/4}$ for the upper bound of the net charge has also been identified in a related model where ground states are subsets of the hexagonal lattice, see [16, Theorem 2.5]. The three theorems are proved in Section 5. Explicit constructions for the upper bound of the ground-state energy and Theorem 2.4(b) are given in Subsection 3.1 and Subsection 3.2, respectively.

Prescribed net charge: We now change the perspective and suppose that the net charge $q_{\rm net}$ is prescribed. We first characterize the energy of $q_{\rm net}$-optimal configurations $\mathcal{E}^n_{\rm min}(q_{\rm net})$, see (2.7). To this end, we introduce the *saturation net charge*

$$q^n_{\rm sat} = \min\left\{q_{\rm net} : \, q_{\rm net} \in \mathcal{Q}_{\rm net}(n) \cap [0,n],\ \mathcal{E}^n_{\rm min}(q_{\rm net}) = -2n + 2q_{\rm net}\right\}. \tag{2.12}$$

The definition corresponds to the smallest net charge for which all atoms of the minority phase are 4-bonded. Configurations with the latter property will be called *saturated* in the following. The saturation net charge can be characterized as follows.

Proposition 2.5 (Characterization of $q^n_{\rm sat}$)**.** *There holds $q^n_{\rm sat} = \phi(n)$, where $\phi(0) = 0$, $\phi(1) = 1$, and*

$$\phi(n) := \begin{cases} 2\left\lfloor -\frac{1}{2} + \frac{1}{2}\sqrt{2n-5}\right\rfloor + 3 & \text{if } n \text{ odd}, n \geq 3, \\ 2\left\lfloor \frac{1}{2}\sqrt{2n-4}\right\rfloor + 2 & \text{if } n \text{ even}, n \geq 2. \end{cases} \tag{2.13}$$

We refer to (6.8) for an equivalent characterization. The representation (2.13) shows the scaling $q^n_{\rm sat} \sim n^{1/2}$, which corresponds to the scaling of the number of boundary atoms of optimal configurations.

By $h^+ := \max(h, 0)$ we denote the positive part of a function h. The energy of $q_{\rm net}$-optimal configurations can be characterized as follows.

Theorem 2.6 (Energy of $q_{\rm net}$-optimal configurations)**.** *For all $n \in \mathbb{N}$ and all $q_{\rm net} \in Q_{\rm net}(n)$ there holds*

$$-2n + 2|q_{\rm net}| \leq \mathcal{E}^n_{\rm min}(q_{\rm net}) \leq -2n + 2|q_{\rm net}| + 4(q^n_{\rm sat} - |q_{\rm net}|)^+. \tag{2.14}$$

We point out that the upper bound in (2.14) is consistent with Theorem 2.1, i.e., with $\mathcal{E}^n_{\rm min}(q_{\rm net}) \geq -\lfloor\beta(n)\rfloor$ for all $q^n_{\rm net}$. To see this, it suffices to note that $2q^n_{\rm sat} \geq -\lfloor -2\sqrt{n}\rfloor$. The result states that for $|q_{\rm net}| \geq q^n_{\rm sat}$, the minimal energy is exactly $-2n + 2|q_{\rm net}|$. This corresponds to the case that optimal configurations are saturated, i.e., each atom of the minority phase is 4-bonded. In this sense, $q^n_{\rm sat}$ can be understood as a critical net charge.

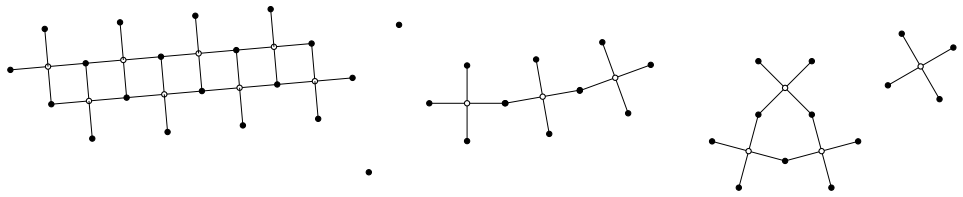

FIGURE 5. *One* $q_{\rm net}$-optimal configuration for $q_{\rm net} > q^n_{\rm sat}$, where $n = 58$, $q^n_{\rm sat} = 12$, $q_{\rm net} = 43 - 15 = 28$.

It turns out that $q^n_{\rm sat}$ is not only a critical net charge in terms of the minimal energy $\mathcal{E}^n_{\rm min}(q_{\rm net})$, but also from a geometrical viewpoint: $q^n_{\rm sat}$ is critical in the sense that beyond $q^n_{\rm sat}$ no crystallization can be expected, cf. Remark 2.7. Note, however, that $q^n_{\rm sat}$-optimal configurations crystallize, cf. Theorem 2.8.

Remark 2.7 (Fragmentation for $q_{\mathrm{net}} > q^n_{\mathrm{sat}}$)**.** For $q_{\mathrm{net}} > q^n_{\mathrm{sat}}$, q_{net}-optimal configurations may be completely degenerate, e.g., may consist of many connected components, see Fig. 5. Their characterizing property is that atoms of the minority phase are 4-bonded with bond angles $\frac{\pi}{2}$, cf. Lemma 4.3(a)(i),(iv).

Recall the definition of diamonds in (2.9).

Theorem 2.8 (Crystallization and Wulff-shape for q^n_{sat}-optimal configurations)**.** *Let $n \in \mathbb{N}$ and let C_n be a q^n_{sat}-optimal configuration.*

(a) *(Crystallization) There exists a universal constant $n_0 \in \mathbb{N}$ independent of n such that C_n is a subset of the square lattice except for at most n_0 atoms.*
(b) *(Wulff-shape) For a universal constant $c > 0$ independent of n, there holds*

$$\min_{a\in\mathbb{R}^2} \#\big(X_n \triangle (a + D_n)\big) \le cn^{3/4}.$$

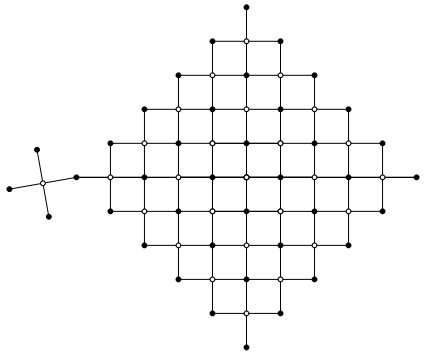

FIGURE 6. A q^n_{sat}-optimal configuration for which four atoms are not subset of the square lattice. (Note that $q^n_{\mathrm{sat}} = 13$ for $n = 65$.)

Complete crystallization cannot be expected for certain values of n, as shown for example in Fig. 6. Comparing this result to the geometry of ground states identified in Theorem 2.3, we observe that the geometry of the Wulff-shape and therefore the global geometry of optimal configurations is very sensitive to the prescribed net charge. Proposition 2.5, Theorem 2.6, and Theorem 2.8 are proved in Section 6. The upper bound for q^n_{sat} is constructed explicitly in Subsection 3.3.

3. Constructions of special subsets of the square lattice

This section is devoted to explicit constructions of sub-configurations of the square lattice with alternating charge distribution. In Subsection 3.1 we exhibit candidates for the ground-state energy which will already give the upper bound in (2.11). In Subsection 3.2 we construct ground-state configurations with net charge of order $n^{1/4}$, which will establish Theorem 2.4(b). Finally, in Subsection 3.3 we define configurations with net charge $\phi(n)$, for which the atoms of the minority phase are 4-bonded. This yields the upper bound for q^n_{sat} in (2.13). We defer the lower bound on the ground-state energy and the upper bound on the net charge to Section 5. The lower bound for q^n_{sat} is addressed in Subsection 6.3.

3.1. Upper bound on the ground-state energy.

This subsection is devoted to an explicit construction of configurations C_n which maximize the number of bonds and that are subsets of the square lattice. These configurations provide a reference energy value for every n, namely $\mathcal{E}(C_n) = -\lfloor \beta(n) \rfloor$.

By the special geometry of the square lattice, it is quite natural to give an interpretation of the two terms appearing in β. The leading order term of the energy is given by $-2n$ which corresponds to the bulk part of the energy. Its value is due to the fact that every interior atom is connected to four other atoms of opposite charge. Furthermore, the repulsive term in the energy is zero for such configurations since the distance of two atoms with the same charge is bigger than or equal to $\sqrt{2}$. The additional lower

order correction term is due to the fact that atoms on the boundary of the ground-state configuration do not have four neighbors.

The construction follows [23] and is illustrated in Fig. 7. If $n = k^2$, $k \in \mathbb{N}$, we arrange the atoms on the lattice points of the square S_n (cf. (2.8)). Then for $n = k^2+m+1$ with $0 \le m \le 2k-1$ we proceed as follows: for $0 \le m \le k-1$ we recursively construct X_{k^2+m+1} by adding the point with coordinates (m, k) to X_{k^2+m}. For $k \le m \le 2k-1$ we construct X_{k^2+m+1} by adding the point with coordinates $(k, m-k)$ to X_{k^2+m}. Since the bond graphs only contain cycles of even length, we can choose corresponding charges such that the resulting configurations C_n have alternating charge distribution. One can check that $\mathcal{Q}(C_n) \in \{-1, 0, 1\}$ for all $n \in \mathbb{N}$.

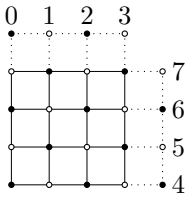

FIGURE 7. The construction for $n = 4^2 + m + 1$ with $0 \le m \le 7$.

Proposition 3.1. *For all $n \in \mathbb{N}$ there holds*

$$\mathcal{E}(C_n) = -\lfloor \beta(n) \rfloor = -\lfloor 2n - \sqrt{2}n \rfloor.$$

Proof. The proof follows as in [23, Proposition 4.3], additionally observing that all atoms in the bond graph are bonded to particles of opposite charge only and that for such configurations, up to neglecting the charge, our energy coincides with the one considered in [23]. □

3.2. **Squares with additional trapezoid.** Recall that the above configurations have net charge in $\{-1, 0, 1\}$. Starting with a square and attaching a trapezoid in a suitable way, we can also construct configurations with energy $-\lfloor \beta(n) \rfloor$ having net charge of order $n^{1/4}$. The construction is inspired by related ideas [8, 16] used in connection to the derivation of the so-called $n^{3/4}$-law.

We choose $k = 5l^2 + 7l + 3$, $l \in 2\mathbb{N}$, and $n = k^2 + 1$. We construct a configuration C_n as follows. We start from the square $S_{(k-l)^2}$. Since $k - l$ is odd, the net charge of $S_{(k-l)^2}$ can be chosen as $+1$. We add a new atom to the bond graph in such a way that it gets bonded to the second up-most among the rightmost atoms. Then we add descendingly atoms along the right side of the square in such a way that they are bonded to the atom in the previous step and one atom of the square. In this way, we add $(k-l-2)$ atoms. Since $k-l$ is odd, we have added $\lceil (k-l)/2 \rceil - 1$ atoms of charge $+1$ and $\lfloor (k-l)/2 \rfloor - 1$ atoms of charge -1. Next, we add a new column starting from the second up-most among the atoms of the previous column. In this way, we add $(k - l - 4)$ atoms. We repeat this procedure until we have added $2l + 1$ columns of atoms. This corresponds to

$$\sum_{j=1}^{2l+1} (k - l - 2j) = 2kl - l^2 + 1$$

added atoms. Note that in each column the number of added atoms of charge $+1$ exceeds the number of added atoms of charge -1 exactly by one, and that the resulting configuration consists of $n = k^2 + 1$ atoms. The construction is sketched in Fig. 8.

We now determine the energy of the configurations. Recall the definition of β in (2.10). We observe that in a column where we add m atoms we add exactly $2m - 1$ bonds to the bond graph. Consequently,

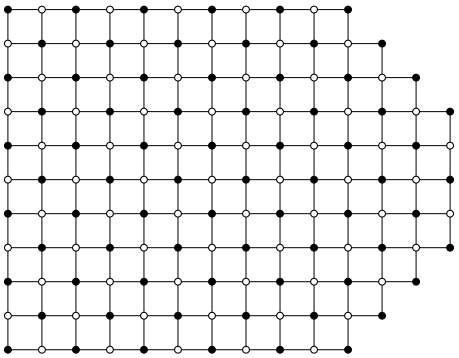

FIGURE 8. Construction of a square with an additional trapezoid. Three columns of atoms have been added where the first and the last atom in the added columns have charge +1. Thus, the net charge is 4. Note that $k = 12$ and $l = 1$ is actually not admissible but chosen here for illustration purposes.

in view of Proposition 3.1, the energy of C_n is given by

$$\begin{aligned}\mathcal{E}(C_n) &= \mathcal{E}(S_{(k-l)^2}) - \sum_{j=1}^{2l+1}(2(k-l-2j)-1) = -2(k-l)^2 + 2(k-l) - 4kl + 2l^2 - 2 + 2l + 1\\ &= -2k^2 + 2\sqrt{k^2} - 1 = -\lfloor\beta(k^2)\rfloor - 1 = -\lfloor\beta(n)\rfloor,\end{aligned}$$

where in the last step we used that $n = k^2 + 1$. We now determine the net charge of the configuration. Recall that the configuration $S_{(k-l)^2}$ has net charge equal to +1. As explained above, in each column the number of added atoms of charge +1 exceeds the number of added atoms of charge −1 by exactly one, i.e., $\mathcal{Q}(C_n) = 2l + 2$.

We are now in the position to give the proof of Theorem 2.4(b). To this end, consider the sequence of integers $n_l = (5l^2 + 7l + 3)^2 + 1$, $l \in 2\mathbb{N}$, and the configuration C_{n_l} constructed above. Note that $4l \geq n_l^{1/4}$. Thus, we obtain $\mathcal{Q}(C_{n_l}) = 2l + 2 \geq \frac{1}{2}n_l^{1/4}$. This yields

$$\liminf_{l\to+\infty} n_l^{-1/4}|\mathcal{Q}(C_{n_l})| > 0.$$

The statement follows once we know that the ground state energy equals exactly $-\lfloor\beta(n)\rfloor$ for all $n \in \mathbb{N}$. This will be proven in Subsection 5.2.

3.3. **Upper bound on q^n_{sat}.** We construct sub-configurations of the square lattice satisfying $\mathcal{E}(C_n) = -2n + 2|\mathcal{Q}(C_n)|$ and $|\mathcal{Q}(C_n)| = \phi(n)$. This shows $q^n_{\text{sat}} \leq \phi(n)$, see (2.12)–(2.13). The main idea of the construction is to place atoms of the minority phase only at sites whose $\mathbb{Z}^2$ neighborhood, that is the set of points on $\mathbb{Z}^2$ with distance 1 to the point, is already occupied by four points of the majority phase. This leads to configurations whose global geometry is reminiscent of a diamond. For an illustration of the construction we refer to Fig. 9.

For $1 \leq n \leq 4$ we arrange n atoms of charge +1 such that their mutual distance is bigger or equal to $\sqrt{2}$. Next, we provide the construction for $n = 1 + 2k^2 + 2k$, $k \in \mathbb{N}$. In this case, we define $X_n = D_n$, see (2.9), and $q_i = (-1)^{i_1+i_2+k}$, $i = (i_1, i_2) \in D_n$. Now for $n = 1 + 2k^2 + 2k + m$, with $1 \leq m \leq 4k + 3$, we recursively construct $X_{1+2k^2+2k+m+1}$ by adding one atom to the configuration X_{1+2k^2+2k+m}. For $m = 1$ we add an atom of positive charge at position $(-(k+1), 1)$. Let $2 \leq m \leq 2k + 2$. For m even, we add an atom of positive charge at position $(-(k+1) + m/2, 1 + m/2)$. For m odd, we add an atom of negative charge at position $(-(k+1) - \lfloor -m/2\rfloor, -\lfloor -m/2\rfloor)$. Now let $2k + 3 \leq m \leq 4k + 3$. For m odd, we add an atom of positive charge at position $(-\lfloor -m/2\rfloor - (k+1), 2k + 3 - \lfloor m/2\rfloor)$. For m even, we add an atom of negative charge at position $(m/2 - (k+2), 2k + 3 - m/2)$.

Proposition 3.2 (Upper bound for q^n_{sat})**.** *Let $n \in \mathbb{N}$. Then $q^n_{\text{sat}} \leq \phi(n)$.*

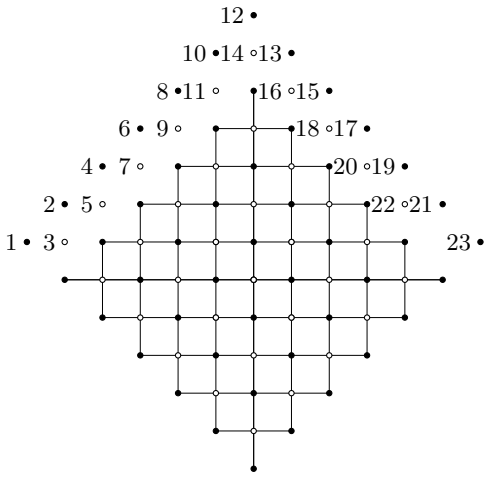

FIGURE 9. The construction of $\phi(n)$-optimal configurations C_n where $n = 1 + 2k^2 + 2k + m$ for $k = 5$ and $1 \le m \le 23$.

Proof. We check that for every $n \in \mathbb{N}$ the constructed configuration C_n satisfies $\mathcal{E}(C_n) = -2n + 2\mathcal{Q}(C_n)$ and $\mathcal{Q}(C_n) = \phi(n)$. This implies $q^n_{\rm sat} \le \phi(n)$.

Let us first confirm that, for all $n \in \mathbb{N}$, C_n satisfies $\mathcal{E}(C_n) = -2n + 2\mathcal{Q}(C_n)$. Recall definition (2.6). Since $\#X_n^+ + \#X_n^- = n$, $\#X_n^+ - \#X_n^- = \mathcal{Q}(C_n)$, and $\#X_n^- \le \#X_n^+$ we get

$$\#X_n^- = \frac{1}{2}(n - \mathcal{Q}(C_n)). \tag{3.1}$$

The construction shows that each atom with negative charge has exactly four neighbors of positive charge since we place atoms of negative charge only on lattice sites whose $\mathbb{Z}^2$-neighbourhood is already occupied by four atoms of positive charge. Moreover, we observe that the distance of atoms with the same charge is at least $\sqrt{2}$. Thus, by [ii], [vii], and (3.1) we get $\mathcal{E}(C_n) = -4\#X_n^- = -2n + 2\mathcal{Q}(C_n)$.

It remains to prove that $\mathcal{Q}(C_n) = \phi(n)$. To this end, it is convenient to use a different representation of ϕ given by

$$\phi(n) = \begin{cases} 2 + 2k + 0 & \text{if } n = 1 + 2k^2 + 2k + m, \quad 1 \le m \le 2k + 2,\ m \text{ odd}, \\ 2 + 2k + 1 & \text{if } n = 1 + 2k^2 + 2k + m, \quad 1 \le m \le 2k + 2,\ m \text{ even}, \\ 3 + 2k + 1 & \text{if } n = 1 + 2k^2 + 2k + m, \quad 2k + 3 \le m \le 4k + 4\ m \text{ odd}, \\ 3 + 2k + 0 & \text{if } n = 1 + 2k^2 + 2k + m, \quad 2k + 3 \le m \le 4k + 4,\ m \text{ even}, \end{cases}$$

see (6.8) in Subsection 6.3 below. Let $n = 1 + 2k^2 + 2k = 1 + 2(k-1)^2 + 2(k-1) + 4(k-1) + 4$. In this case, C_n is a union of $2k + 1$ rows for each of which the number of atoms of charge $+1$ exceeds the number of atoms of charge -1 by exactly one. We therefore have $\mathcal{Q}(C_n) = 1 + 2k = \phi(n)$.

For $n = 1+2k^2+2k+m$ with $m \in \{1, 2\}$ we add m atoms of charge $+1$ to the configuration C_{1+2k^2+2k}. Consequently, we get $\mathcal{Q}(C_n) = \mathcal{Q}(C_{1+2k^2+2k}) + m = 1 + 2k + m = \phi(n)$.

For $3 \le m \le 2k+2$ we add alternatingly first an atom of charge -1 and then an atom of charge $+1$. We therefore obtain $\mathcal{Q}(C_n) = \mathcal{Q}(C_{1+2k^2+2k})+1 = 1+2k+1 = \phi(n)$ if m is odd and $\mathcal{Q}(C_n) = \mathcal{Q}(C_{1+2k^2+2k})+2 = 1+2k+2 = \phi(n)$ if m is even. For $2k+3 \le m \le 4k+3$ we add alternatingly first an atom of charge $+1$ and then an atom of charge -1. We therefore obtain $\mathcal{Q}(C_n) = \mathcal{Q}(C_{1+2k^2+4k+2})+1 = 1+2k+3 = \phi(n)$ if m is odd and $\mathcal{Q}(C_n) = \mathcal{Q}(C_{1+2k^2+4k+2}) = 1 + 2k + 2 = \phi(n)$ if m is even. □

4. Elementary properties of optimal configurations

In this section we prove elementary geometric properties of optimal configurations.

Lemma 4.1. *Let C_n be an optimal configuration. Then C_n has alternating charge distribution and*

$$\#\mathcal{N}(x_i) \leq 4 \text{ for all } i \in \{1,\dots,n\}. \tag{4.1}$$

Proof. In this proof, we will use the following convention: we say that we *relocate* $(x,q) \in C_n$, and write $C_n - \{(x,q)\}$, by considering the configuration $(C_n \cup (x+\tau,q)) \setminus (x,q)$, where $\tau \in \mathbb{R}^2$ is chosen such that

$$\operatorname{dist}(X_n, x+\tau) \geq \sqrt{2}.$$

Since C_n is a q_{net}-optimal configuration, there holds $\mathcal{E}(C_n) < +\infty$. Thus, by [i] and [iv]

$$\operatorname{dist}(x_i, X_n \setminus \{x_i\}) \geq 1 \text{ for all } i \in \{1,\dots,n\}. \tag{4.2}$$

For brevity, we define $\mathcal{N}_{\text{rep}}(x_i) = \mathcal{N}(x_i) \cap \{x_j \in X_n : q_j = q_i\}$ for all $i \in \{1,\dots,n\}$. We give the proof of the statement in two steps.

Step 1: $\#\mathcal{N}_{\text{rep}}(x_i) = 0$ for all $i \in \{1,\dots,n\}$. First, (4.2) and $r_0 < (2\sin(\frac{\pi}{7}))^{-1}$ entail by an elementary argument that

$$\#\mathcal{N}(x_i) \leq 6 \text{ for all } i \in \{1,\dots,n\}. \tag{4.3}$$

Indeed, if $\#\mathcal{N}(x_i) \geq 7$, two neighbors of x_i would necessarily have distance smaller than 1. Now assume by contradiction that $\#\mathcal{N}_{\text{rep}}(x_i) \geq 1$. Note that every bond between atoms of different charge contributes at least -1 to the energy by [ii]. This along with $V_{\text{r}} \geq 0$ and the fact that the energy per neighbor of same charge exceeds 6 (see [iv], [v], and [vi]) allows us to relocate (x_i, q_i): by (4.3) we obtain

$$\begin{aligned}\mathcal{E}(C_n - \{(x_i,q_i)\}) &< \mathcal{E}(C_n) + \#\left(\mathcal{N}(x_i) \setminus \mathcal{N}_{\text{rep}}(x_i)\right) - 6\#\mathcal{N}_{\text{rep}}(x_i)\\ &\leq \mathcal{E}(C_n) + 5 - 6 < \mathcal{E}(C_n).\end{aligned}$$

This contradicts the fact that C_n is a q_{net}-optimal configuration. Thus, Step 1 is proved.

Step 2: $\#\mathcal{N}(x_i) \leq 4$ for all $i \in \{1,\dots,n\}$. Assume by contradiction that there exists $i \in \{1,\dots,n\}$ such that $\#\mathcal{N}(x_i) \geq 5$. By Step 1 we may suppose that there exist $\{x_0,\dots,x_4\} \subset \mathcal{N}(x_i)$ with $q_j = -q_i$ $j = 0,\dots,4$. We let $\theta_j \in [0,2\pi)$ be the angle between x_j, x_i, x_{j+1}. (Here and in the following the indices have to be understood modulo 4.) We can choose $j_0 \in \{0,\dots,4\}$ such that

$$\theta_{j_0} \leq \frac{1}{5}\sum_{j=0}^{4}\theta_j = \frac{2\pi}{5}.$$

Since $\sin(x)$ is increasing for $x \in [0,\frac{\pi}{2}]$, we have $|x_{j_0} - x_{j_0+1}| \leq 2r_0\sin(\theta_{j_0}/2) \leq 2r_0\sin(\pi/5)$. By using [ii], [vi], $V_{\text{r}} \geq 0$ (cf. [iv]), and (4.3) we finally get

$$\begin{aligned}\mathcal{E}(C_n - \{(x_{j_0},q_{j_0})\}) &\leq \mathcal{E}(C_n) - V_{\text{r}}(2r_0\sin(\pi/5)) + \#\big(\mathcal{N}(x_{j_0}) \setminus \mathcal{N}_{\text{rep}}(x_{j_0})\big)\\ &< \mathcal{E}(C_n) - 6 + 6 = \mathcal{E}(C_n).\end{aligned}$$

This contradicts the fact that C_n is an optimal configuration and concludes the proof of Step 2.

Now (4.1) follows from Step 2. The property of alternating charge (see (2.4)) follows from Step 1. This concludes the proof of Lemma 4.1. □

Lemma 4.2 (Bond-angles and polygons)**.** *Let C_n be a configuration.*

(a) *If C_n is an optimal configuration, then the bond graph consists only of polygons of even length. For each polygon $P \subset X_n$ satisfying $\mathcal{A}(X_n) \cap P \neq \emptyset$ there holds*

$$\#(\mathcal{A}(X_n) \cap P) \geq 2.$$

(b) *If C_n is such that $\mathcal{E}(C_n) = -b$, then all bonds have unit length, the configuration is repulsion-free, and all bond angles θ satisfy*

$$\tfrac{\pi}{2} \leq \theta \leq \tfrac{3\pi}{2}. \tag{4.4}$$

In particular, all squares in the bond graph are regular.

Proof. Proof of (a). Let C_n be an optimal configuration. By Lemma 4.1 the configuration has alternating charge distribution. Hence, the bond graph consists only of elementary polygons of even length. Let $P = \{x_1, \dots, x_k\} \subset X_n$ be a polygon, and denote the interior angles by $\{\theta_1, \dots, \theta_k\}$. Assume by contradiction that $\#(\mathcal{A}(X_n) \cap P) = 1$. Without loss of generality $x_1 \in \mathcal{A}(X_n)$, i.e. $\theta_1 \notin \frac{\pi}{2}\mathbb{N}$. We have $\theta_1 = \pi(k-2) - \sum_{i=2}^k \theta_i$. Now by assumption $\theta_i \in \frac{\pi}{2}\mathbb{N}$ for all $i \in \{2, \dots, k\}$ and so the right hand side is an integer multiple of $\frac{\pi}{2}$. This contradicts the fact that $x_1 \in \mathcal{A}(X_n)$.

Proof of (b): Given a configuration C_n such that $\mathcal{E}(C_n) = -b$, all bonds are necessarily of unit length and the configuration is repulsion-free, see Remark 2.2. We show that all bond angles θ satisfy (4.4). In fact, suppose that x_1, x_0, x_2 form the angle θ. Observe that C_n has alternating charge distribution since it is repulsion-free. As x_1 and x_2 are neighbors of x_0, we thus have $q_1 = q_2$. Then we get $|x_1 - x_0| = |x_2 - x_0| = 1$ as well as $|x_1 - x_2| \geq \sqrt{2}$ by [vii]. A simple geometric argument yields $\pi/2 \leq \theta \leq 3\pi/2$. By (4.4) and the fact that the four interior angles of a square sum up to 2π we deduce that all squares are regular. □

We now investigate the relation of net charge and energy. Without restriction we consider configurations with non-negative net charge in order to simplify notation.

Lemma 4.3 (Net charge controls energy)**.** *Let C_n be a configuration with $\mathcal{Q}(C_n) \geq 0$.*
(a) There holds

$$\mathcal{E}(C_n) \geq -2n + 2\mathcal{Q}(C_n), \tag{4.5}$$

with equality only if

(i) *All atoms with charge -1 are 4-bonded, and all bonds are of unit length,*
(ii) *The configuration is repulsion-free,*
(iii) $\mathcal{Q}(C_n) \geq q^n_{\rm sat}$,
(iv) *All 4-bonded atoms have only bond angles $\frac{\pi}{2}$,*
(v) *If x_i satisfies $\#\mathcal{N}(x_i) = 3$, then $x_i \notin \mathcal{A}(X_n)$.*
(vi) *For all connected components $C_m \subset C_n$ there holds $\mathcal{Q}(C_m) \geq q^m_{\rm sat}$.*

(b) Conversely, if properties (i) and (ii) are satisfied, then equality holds in (4.5).

Proof. We first show (4.5). To this end, it is not restrictive to assume that C_n is an optimal configuration. Recall (2.6). Since $\#X_n^+ + \#X_n^- = n$ and $\#X_n^+ - \#X_n^- = \mathcal{Q}(C_n)$, we get $\min\{\#X_n^+, \#X_n^-\} = (n - |\mathcal{Q}(C_n)|)/2$. As C_n is an optimal configuration, Lemma 4.1 yields $\mathcal{N}(x_i) \leq 4$ for all $i = 1, \dots, n$. We therefore obtain by [ii] and $V_{\rm r} \geq 0$

$$\mathcal{E}(C_n) \geq -b \geq -4\,\min\{\#X_n^+, \#X_n^-\} = -2n + 2|\mathcal{Q}(C_n)|. \tag{4.6}$$

This shows (4.5) since by assumption $|\mathcal{Q}(C_n)| = \mathcal{Q}(C_n)$. In a similar fashion, to see (b), it suffices to note that (i) and (ii) imply that all inequalities in (4.6) are actually equalities.

Now we assume that equality holds in (4.5). (In particular, this implies that C_n is an optimal configuration.) We confirm (i)–(vi).

Proof of (i): Suppose that there exists an atom with charge -1 such that $\mathcal{N}(x_i) < 4$. This implies strict inequality in the second inequality in (4.6). If on the other hand there exists a bond that is not of unit length, we obtain a strict inequality in the first inequality in (4.6), see [ii]. In both cases, we get a contradiction to the equality in (4.5).

Proof of (ii): If the configuration is not repulsion-free, we have strict inequality in the first inequality in (4.6) by Remark 2.2. This again contradicts equality in (4.5).

Proof of (iii): The inequality follows directly from definition (2.12).

Proof of (iv), (v): Now, (iv) follows from (4.4) and the fact that the bond angles at each atom sum up to 2π. To see (v), let x_0 be a 3-bonded atom. By (i) it necessarily has charge $+1$ and it is only bonded to atoms with charge -1. These atoms are 4-bonded by (i). Denote the bond angles at x_0 by $\theta_1, \theta_2, \theta_3$. Without loss of generality, suppose that $\pi/2 \leq \theta_1 \leq 2\pi/3 \leq 3\pi/4$, see (4.4). Assume by contradiction

that $\theta_1 > \pi/2$. Denote by x_1, x_2 the two 4-bonded atoms whose bonds enclose θ_1. Denote by z_1, z_2 the two atoms $z_1 \in \mathcal{N}(x_1) \setminus \{x_0\}$, $z_2 \in \mathcal{N}(x_2) \setminus \{x_0\}$ that have minimal distance to each other. Observe that z_1 and z_2 have charge $+1$. We proceed to show that $z_1 \neq z_2$ and $|z_1 - z_2| < \sqrt{2}$ which contradicts (ii). By (iii) and the fact that all bonds are of unit length we get $|z_1 - x_0| = |z_2 - x_0| = \sqrt{2}$. Moreover, the angle enclosed by z_1, x_0, z_2 is equal to $\theta_1 - 2\pi/4$, where $0 < \theta_1 - 2\pi/4 \leq \pi/4$. Thus, we obtain

$$0 < |z_1 - z_2| = 2\sqrt{2} \sin\left(\frac{1}{2}\left(\theta_1 - \frac{\pi}{2}\right)\right) \leq 2\sqrt{2} \sin\left(\frac{\pi}{8}\right) < \sqrt{2}.$$

This yields $z_1 \neq z_2$ and contradicts (ii). Therefore, we have shown $\theta_1 = \pi/2$. One of the remaining two bond angles, say θ_2, then also satisfies $\theta_2 \leq 3\pi/4$. By the same argument we have that $\theta_2 = \pi/2$. Now $\theta_3 = \pi$ and the claim is proved.

Proof of (vi): Assume that there exist two connected components C_m and C_{n-m} with no bonds between them. We have that

$$\mathcal{Q}(C_m) + \mathcal{Q}(C_{n-m}) = \mathcal{Q}(C_n). \tag{4.7}$$

By (4.6) applied to C_m and C_{n-m} there holds

$$\mathcal{E}(C_m) \geq -2m + 2|\mathcal{Q}(C_m)|, \qquad \mathcal{E}(C_{n-m}) \geq -2(n-m) + 2|\mathcal{Q}(C_{n-m})|, \tag{4.8}$$

and therefore

$$-2n + 2|\mathcal{Q}(C_n)| = \mathcal{E}(C_n) \geq -2n + 2(|\mathcal{Q}(C_m)| + |\mathcal{Q}(C_{n-m})|) \geq -2n + 2|\mathcal{Q}(C_n)|. \tag{4.9}$$

We now have equality everywhere in (4.9) and therefore necessarily also in (4.8). Moreover, in view of (4.7), equality also implies that there holds $\mathcal{Q}(C_m) \geq 0$ and $\mathcal{Q}(C_{n-m}) \geq 0$. By equality in (4.8) and (iii) we get $\mathcal{Q}(C_m) \geq q_{\mathrm{sat}}^m$ and $\mathcal{Q}(C_{n-m}) \geq q_{\mathrm{sat}}^{n-m}$. □

5. Characterization of ground states

This section is devoted to the proofs of Theorem 2.1, Theorem 2.3, and Theorem 2.4.

5.1. **Boundary energy.** This subsection is devoted to the concept of boundary energy and a corresponding estimate which will be instrumental for the characterization of ground states and their energy in Subsections 5.2 and 5.3. It is convenient to first introduce an auxiliary energy, sorted by the contributions of single atoms. We then define the so-called boundary energy in terms of this auxiliary energy.

Reduced energy: Let C_n be a configuration and let $x_i \in X_n$. We set

$$V_{\mathrm{atom}}(x_i) := \frac{1}{2} \sum_{x_j \in \mathcal{N}(x_i)} V_{\mathrm{a}}(|x_i - x_j|) + \frac{1}{8} \sum_{\substack{x_j, x_k \in \mathcal{N}(x_i) \\ x_j \neq x_k}} V_{\mathrm{r}}(|x_j - x_k|). \tag{5.1}$$

where $\mathcal{N}(x_i)$ is defined in (2.2). We define the *reduced energy* $\mathcal{R} : (\mathbb{R}^2 \times \{-1, 1\})^n \to \overline{\mathbb{R}}$ by

$$\mathcal{R}(C_n) := \sum_{x_i \in X_n} V_{\mathrm{atom}}(x_i). \tag{5.2}$$

Lemma 5.1 (Relation of $\mathcal{E}$ and $\mathcal{R}$)**.** *If C_n has alternating charge distribution and satisfies $\#\mathcal{N}(x_i) \leq 4$ for all $i = 1, \ldots, n$, then*

$$\mathcal{E}(C_n) \geq \mathcal{R}(C_n)$$

with equality if C_n is repulsion-free.

Proof. Since C_n has alternating charge distribution, the contributions of V_{a} in (2.1) and (5.2) coincide. In the case that C_n is repulsion-free, the contributions of V_{r} vanish and thus there indeed holds $\mathcal{E}(C_n) = \mathcal{R}(C_n)$. In the general case, we observe that in (2.1) each pair $\{x_i, x_j\}$ with $q_i = q_j$ contributes $V_{\mathrm{r}}(|x_i - x_j|)$ to the energy. In (5.2), however, $\{x_i, x_j\}$ contributes at most $V_{\mathrm{r}}(|x_i - x_j|)$ since the pair appears at most

eight times in the sum. This is due to double counting and the fact that each atom can be bonded to at most four other atoms. □

By Lemma 4.1, ground states C_n satisfy the assumptions of the lemma. Later we will also see that ground states are repulsion-free which will imply $\mathcal{E}(C_n) = \mathcal{R}(C_n)$.

Boundary atoms, boundary energy: Within the bond graph, we say that an atom is a *boundary atom* if it is not contained in the interior region of any simple cycle. Otherwise, we call it *bulk atom*. We denote the union of the boundary atoms by ∂X_n and let $d = \#\partial X_n$. A *boundary bond* is a bond containing a boundary atom. All other bonds are called *bulk bonds*. Given C_n, we define its *bulk*, denoted by $C_n^{\rm bulk}$, as the sub-configuration obtained by dropping all boundary atoms (and the corresponding charges). Similarly, the particle positions are indicated by $X_n^{\rm bulk}$. With the above definition, we have that the bulk is an $(n-d)$-atom configuration. There are two contributions to the energy of C_n, namely $\mathcal{R}^{\rm bnd}$ and $\mathcal{R}^{\rm bulk}$, defined by

$$\begin{aligned} \mathcal{R}^{\rm bulk}(C_n) &:= \mathcal{R}(C_n^{\rm bulk}), \\ \mathcal{R}^{\rm bnd}(C_n) &:= \mathcal{R}(C_n) - \mathcal{R}^{\rm bulk}(C_n). \end{aligned} \tag{5.3}$$

Remark 5.2 (Boundary energy)**.** Since $C_n^{\rm bulk}$ does not contain boundary bonds of C_n, each boundary bond $\{x_i, x_j\}$ with $q_i \neq q_j$ contributes $V_{\rm a}(|x_i - x_j|)$ to $\mathcal{R}^{\rm bnd}(C_n)$, and each boundary bond $\{x_i, x_j\}$ with $q_i = q_j$ contributes at least $\frac{1}{4}V_{\rm r}(|x_i - x_j|)$ to $\mathcal{R}^{\rm bnd}(C_n)$. Note that $\mathcal{R}^{\rm bnd}(C_n)$ contains also pair interactions of certain bulk bonds, namely if the corresponding bulk atoms are neighbors of the same boundary atom, see Fig. 10. We point out that, when the boundary energy in (5.3) is defined with $\mathcal{E}$ in place of $\mathcal{R}$ (see, e.g., [16, 23, 25]), such pair interactions do not contribute to the boundary energy. Our definition, slightly different in comparison to [16], is necessary from a technical point of view in order to derive the 'correct' boundary energy estimate (5.4) and to obtain (5.6)-(5.7) as necessary conditions for equality in (5.4).

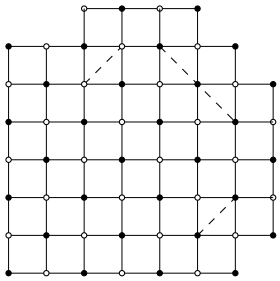

FIGURE 10. The dashed bonds contribute to $\mathcal{R}^{\rm bnd}$. They would not contribute to the boundary energy if it was defined with $\mathcal{E}$ in place of $\mathcal{R}$.

Maximal polygon: We introduce an additional notion in the case that C_n is connected and does not contain acyclic bonds. In this case, the bond graph is delimited by a simple cycle which we call the *maximal polygon*. We denote the atoms of the maximal polygon by $\{x_1, \dots, x_d\}$ and the interior angle at $x_i \in \partial X_n$ by θ_i. Moreover, for $2 \le k \le 4$, we indicate by

$$I_k = \{x_i \in \partial X_n : \#\mathcal{N}(x_i) = k\},$$

the set of k-bonded boundary atoms. For ground states C_n there holds $\#I_2 + \#I_3 + \#I_4 = d$ by Lemma 4.1.

We now provide an estimate for the boundary energy $\mathcal{R}^{\rm bnd}$. Its proof is inspired by [23, Lemma 3.1]. The precise estimates, however, deviate significantly from [23] due to the presence of the repulsive potential $V_{\rm r}$ instead of an angular potential. We defer the proof to Appendix A.

Lemma 5.3. *Let $n \geq 4$ and let C_n be a connected ground state with no acyclic bonds. Then*

$$\mathcal{R}^{\mathrm{bnd}}(C_n) \geq -2d + 4 \tag{5.4}$$

with equality only if the following conditions are satisfied:

$$\text{All boundary bonds are of unit length,} \tag{5.5}$$

$$\#I_2 + 2\#I_3 + 3\#I_4 = 2d - 4, \tag{5.6}$$

$$\theta_i = \frac{\pi}{2} \ \text{ for } x_i \in I_2, \qquad \theta_i = \pi \ \text{ for } x_i \in I_3, \qquad \theta_i = \frac{3\pi}{2} \ \text{ for } x_i \in I_4. \tag{5.7}$$

Remark 5.4. Observe by (5.6) that equality in (5.4) implies that $2d-4$ bonds contribute to the boundary energy. Thus, equality in (5.4) together with [ii] and [vii] imply that for all boundary atoms x_i one has $\min\{|x_i - x_j| : \ j \in \{1, \dots, n\}, j \neq i, \ q_j = q_i\} \geq \sqrt{2}$.

Recall the excess of edges $\eta = \sum_{j\geq 4}(j-4)f_j$, introduced in (2.3), where f_j denotes the number of polygons with j vertices in the bond graph. Clearly, $\eta = 0$ if and only if the bond graph consists of squares only. We also recall that b denotes the number of bonds in the bond graph.

Lemma 5.5 (Cardinality of the bulk)**.** *Let C_n be a connected ground state with no acyclic bonds. Then*

$$n - d = 2b + 4 - 3n + \eta.$$

Proof. Let f_j be the number elementary j-gons in the bond graph and let f be the number of elementary polygons in the bond graph. From Lemma 4.2(a) we obtain

$$\sum_{j\geq 4} j f_j = 2b - d,$$

since by the summation on the left all bonds contained in the maximal polygon are counted only once whereas all other bonds are counted twice. By (2.3) we get $4f = 2b - d - \eta$. This along with Euler's formula $n - b + f = 1$ (omitting the exterior face) yields $n - d = 2b + 4 - 3n + \eta$. □

5.2. **Energetic characterization.** We start with the proof of Theorem 2.1. We use the following properties of the function β defined in (2.10).

Lemma 5.6. *The function $\beta : \mathbb{N} \to \mathbb{R}$ satisfies*

(i) $\lfloor \beta(n-m) \rfloor + \lfloor \beta(m) \rfloor + 1 < \lfloor \beta(n) \rfloor$ *for all $n \geq 4$ and $1 \leq m, n-m \leq n$,*
(ii) $\lfloor \beta(n) \rfloor + 1 \leq \lfloor \beta(n+1) \rfloor$ *for all $n \geq 1$.*

Proof. See [23, Proposition 4.1, Proposition 4.2]. □

Lemma 5.7. *Let $j, n, m \in \mathbb{N}$ and let $x \in \mathbb{R}$ satisfy*

$$2 - \frac{3}{2}n + \frac{m}{2} \geq x \geq -2n + j + 2\sqrt{-2x + 4 - 3n + m}.$$

Then $x \geq -2n + j - 4 + 2\sqrt{m + n + 8 - 2j}$.

Proof. The proof is elementary: we note that the function

$$x \mapsto x + 2n - j - 2\sqrt{-2x + 4 - 3n + m}$$

is strictly increasing and vanishes for $x = -2n + j - 4 + 2\sqrt{m + n + 8 - 2j}$. □

Proof of Theorem 2.1. We start by noting that every ground state C_n has alternating charge distribution and every atom has at most four neighbors by Lemma 4.1. By Proposition 3.1 and Lemma 5.1 the ground-state energy satisfies

$$\mathcal{R}(C_n) \leq \mathcal{E}(C_n) \leq -\lfloor \beta(n) \rfloor. \tag{5.8}$$

We prove that, if C_n is a ground state, then C_n is connected, does not contain bridges, and satisfies

$$\mathcal{R}(C_n) = -b = -\lfloor \beta(n) \rfloor. \tag{5.9}$$

The same statement then holds also for $\mathcal{E}(C_n)$. In fact, due to (5.8)-(5.9), we have

$$-\lfloor \beta(n) \rfloor = \mathcal{R}(C_n) \le \mathcal{E}(C_n) \le -\lfloor \beta(n) \rfloor.$$

This implies $\mathcal{E}(C_n) = \mathcal{R}(C_n) = -b = -\lfloor \beta(n) \rfloor$.

Let $n \ge 4$. We proceed by induction. Suppose that the statement has been proven for all $m < n$ (for $1 \le m \le 3$ this is elementary). We first show connectedness of the ground state and the non-existence of bridges (Step 1). Afterwards, we prove the energy equality (Step 2).

Step 1: C_n is connected and does not contain bridges. Assume by contradiction that C_n consists of two sub-configurations C_m and C_{n-m} that are connected by at most one bond. The energy contribution of this bond, if it exists, is greater or equal to -1. Apart from that, we can estimate the sum of the energy contributions of both components separately. In both cases, as $m, n-m < n$ $n \ge 4$, using the induction assumption, Lemma 5.6(i), and $V_{\rm r} \ge 0$ (cf. [iv]), we get

$$\mathcal{R}(C_n) \ge \mathcal{R}(C_m) + \mathcal{R}(C_{n-m}) - 1 \ge -\lfloor \beta(m) \rfloor - \lfloor \beta(n-m) \rfloor - 1 > -\lfloor \beta(n) \rfloor.$$

This contradicts (5.8) and shows that C_n is connected and its bond graph does not contain any bridges.

Step 2: Energy equality $\mathcal{R}(C_n) = -b = -\lfloor \beta(n) \rfloor$. We divide the proof into three steps. We first treat the case that C_n contains acyclic bonds (Step 2.1). Afterwards, we consider only configurations C_n without acyclic bonds and show $\mathcal{R}(C_n) = -b$ (Step 2.2) as well as $\mathcal{R}(C_n) = -\lfloor \beta(n) \rfloor$ (Step 2.3).

Step 2.1: C_n contains acyclic bonds. By Step 1, C_n does not contain bridges. If there exist flags, we can find an atom x_i such that removing x_i removes exactly one flag. We can count the energy contribution of this flag by at least -1 and we estimate the energy of the rest of the configuration by induction. By Lemma 5.6(ii) we get

$$\mathcal{R}(C_n) \ge -1 + \mathcal{R}(C_n \setminus \{(x_i, q_i)\}) \ge -1 - \lfloor \beta(n-1) \rfloor \ge -\lfloor \beta(n) \rfloor.$$

Equality also shows that $C_n \setminus \{(x_i, q_i)\}$ has $\lfloor \beta(n-1) \rfloor$ bonds by induction and C_n has $\lfloor \beta(n-1) \rfloor + 1 = \lfloor \beta(n) \rfloor$ bonds.

Step 2.2: $\mathcal{R}(C_n) = -b$ for connected C_n with no acyclic bonds. Assume by contradiction that $\mathcal{R}(C_n) > -b$, i.e., there exist $x_1, x_2 \in X_n$ such that $q_1 = q_2$ and $|x_1 - x_2| < \sqrt{2}$ or there exists a bond between $x_1, x_2 \in X_n$ such that $q_1 = -q_2$ and $|x_1 - x_2| > 1$. Now if $x_1 \in \partial X_n$ or $x_2 \in \partial X_n$ we have by (5.4), (5.5), and Remark 5.4

$$\mathcal{R}^{\rm bnd}(C_n) > -2d + 4.$$

Moreover, by (5.3), the induction hypothesis, and (5.9) there holds

$$\mathcal{R}^{\rm bulk}(C_n) = \mathcal{R}(C_n^{\rm bulk}) \ge -\lfloor \beta(n-d) \rfloor.$$

On the other hand, if $x_1, x_2 \notin \partial X_n$, by Lemma 5.3 we get $\mathcal{R}^{\rm bnd}(C_n) \ge -2d + 4$. By (5.3) and the induction assumption we obtain

$$\mathcal{R}^{\rm bulk}(C_n) = \mathcal{R}(C_n^{\rm bulk}) > -\lfloor \beta(n-d) \rfloor.$$

In both cases, by (5.3) and (2.10) there holds $\mathcal{R}(C_n) > -\lfloor 2n - 2\sqrt{(n-d)} \rfloor + 4$. Since the right hand side is an integer, we obtain

$$-(\lfloor -\mathcal{R}(C_n) \rfloor + 1) \ge -2n + 2\sqrt{(n-d)} + 4. \tag{5.10}$$

In a similar fashion, the assumption $\mathcal{R}(C_n) > -b$ implies $-\lfloor -\mathcal{R}(C_n) \rfloor - 1 \ge -b$. Now by Lemma 5.5 we obtain $n - d \ge 2(\lfloor -\mathcal{R}(C_n) \rfloor + 1) + 4 - 3n$. This along with (5.10) yields

$$-(\lfloor -\mathcal{R}(C_n) \rfloor + 1) \ge -2n + 2\sqrt{2(\lfloor -\mathcal{R}(C_n) \rfloor + 1) + 4 - 3n} + 4.$$

Note that $-(\lfloor -\mathcal{R}(C_n)\rfloor+1) \leq 2-3/2n$. By using Lemma 5.7 with $j=4, m=0$, and $x=-(\lfloor -\mathcal{R}(C_n)\rfloor+1)$ we obtain

$$-(\lfloor -\mathcal{R}(C_n)\rfloor+1) \geq -2n+2\sqrt{n}.$$

Since the left hand side is an integer, we get by (2.10)

$$\mathcal{R}(C_n) > -(\lfloor -\mathcal{R}(C_n)\rfloor+1) \geq -\lfloor 2n-2\sqrt{n}\rfloor = -\lfloor \beta(n)\rfloor.$$

This contradicts (5.8).

Step 2.3: $\mathcal{R}(C_n) = -\lfloor\beta(n)\rfloor$ for connected C_n with no acyclic bonds. Due to (5.8), it suffices to prove $\mathcal{R}(C_n) \geq -\lfloor\beta(n)\rfloor$. We again proceed by induction. By Lemma 5.3, (5.3), and the induction hypothesis we obtain

$$\mathcal{R}^{\mathrm{bnd}}(C_n) \geq -2d+4, \qquad \mathcal{R}^{\mathrm{bulk}}(C_n) = \mathcal{R}(C_n^{\mathrm{bulk}}) \geq -\lfloor\beta(n-d)\rfloor.$$

By (2.10) and (5.3) there holds $\mathcal{R}(C_n) \geq -2n+2\sqrt{n-d}+4$. By Lemma 5.5 and Step 2.2 we obtain $n-d \geq -2\mathcal{R}(C_n)+4-3n$. This yields

$$\mathcal{R}(C_n) \geq -2n+2\sqrt{-2\mathcal{R}(C_n)-3n+4}+4.$$

By applying Lemma 5.7 with $j=4$, $m=0$, and $x=\mathcal{R}(C_n)$ we obtain $\mathcal{R}(C_n) \geq -\beta(n)$. Finally, since $\mathcal{R}(C_n)$ is an integer due to Step 2.2, we conclude $\mathcal{R}(C_n) \geq -\lfloor\beta(n)\rfloor$. □

5.3. **Geometric Characterization.** We now proceed with the proof of Theorem 2.3. To this end, we first prove two lemmas about flags and non-equilibrated atoms.

Lemma 5.8 (Flags)**.** *Let $n \geq 4$ and let C_n be a ground state. Then the bond graph of C_n contains at most one flag.*

Proof. Assume by contradiction that there exist at least two flags. We can choose two flags such that removing the two flags increases the energy of the configuration at most by 2. By applying Thereom 2.1 to the sub-configuration after removing the two flags, we obtain $\mathcal{E}(C_n) \geq -2-\lfloor\beta(n-2)\rfloor$. Therefore, we get by (2.10)

$$\begin{aligned}\mathcal{E}(C_n) &\geq -2-2(n-2)+2\sqrt{n-2} = -2n+2\sqrt{n}-2\sqrt{n}+2+2\sqrt{n-2}\\ &= -2n+2\sqrt{n}+2-\frac{4}{\sqrt{n-2}+\sqrt{n}}.\end{aligned}$$

We have that $2-\frac{4}{\sqrt{n-2}+\sqrt{n}} \geq 1$ for all $n \geq 6$. With the above estimate this implies $\mathcal{E}(C_n) > -\lfloor\beta(n)\rfloor$. This gives a contradiction to Theorem 2.1 in the cases $n \geq 6$. For $n=4,5$ it can be checked directly that $-2-\lfloor\beta(n-2)\rfloor > -\lfloor\beta(n)\rfloor$. □

Recall the definition of non-equilibrated atoms in Subsection 2.2. By $\mathcal{A}_{\mathrm{bulk}}(X_n) \subset \mathcal{A}(X_n)$ we additionally denote the bulk atoms which are not equilibrated.

Lemma 5.9 (Non-equilibrated atoms)**.** *Let C_n be a ground state and assume that its bond graph does not contain any acyclic bonds. If $\mathcal{A}(X_n) \neq \emptyset$, then $\#\mathcal{A}(X_n) \geq 2$ and $\eta \geq 2$. If $\mathcal{A}_{\mathrm{bulk}}(X_n) \neq \emptyset$, then $\#\mathcal{A}(X_n) \geq 2$ and $\eta \geq 4$.*

Proof. We split the proof into several steps. First, we prove that $\theta \in [\frac{\pi}{2}, \frac{3\pi}{2}]$ for all bond angles θ. Secondly, we show that, if $\mathcal{A}(X_n) \neq \emptyset$, then $\#\mathcal{A}(X_n) \geq 2$. Then we prove $\eta \geq 2$ if $\mathcal{A}(X_n) \neq \emptyset$. Finally, we confirm that, if $\mathcal{A}_{\mathrm{bulk}}(X_n) \neq \emptyset$, then $\eta \geq 4$. These statements show the thesis of the lemma.

Step 1: $\theta \in [\frac{\pi}{2}, \frac{3\pi}{2}]$ for all bond angles θ. By Theorem 2.1 there holds $\mathcal{E}(C_n) = -b$. Thus, Lemma 4.2(b) implies that $\theta \in [\frac{\pi}{2}, \frac{3\pi}{2}]$ for all bond angles θ.

Step 2: If $\mathcal{A}(X_n) \neq \emptyset$, then $\#\mathcal{A}(X_n) \geq 2$. Since the bond graph of C_n does not contain any acyclic bonds and $\mathcal{A}(X_n) \neq \emptyset$, there holds $\mathcal{A}(X_n) \cap P \neq \emptyset$ for some polygon P in the bond graph. By Lemma 4.2(a) it follows that $\#(\mathcal{A}(X_n) \cap P) \geq 2$.

Step 3: If $\mathcal{A}(X_n) \neq \emptyset$, then $\eta \geq 2$. Assume by contradiction that $\eta = 0$. By the definition of η this implies that all elementary polygons in the bond graph are squares. Furthermore, since the bond graph of C_n does not contain any acyclic bonds, all atoms are contained in some elementary polygon, i.e., in some square. Lastly, we note that, due to Theorem 2.1, there holds $\mathcal{E}(C_n) = -b$ and therefore by Lemma 4.2(b) all squares are regular. In particular, all their atoms are equilibrated. This contradicts the fact that $\mathcal{A}(X_n) \neq \emptyset$.

Step 4: If $\mathcal{A}_{\rm bulk}(X_n) \neq \emptyset$, then $\eta \geq 4$. Let $x \in \mathcal{A}_{\rm bulk}(X_n)$ and denote by $\theta_1, \dots, \theta_k$ the bond angles at x. By Lemma 4.1 we have that $k \leq 4$. We have $k \in \{2, 3, 4\}$. We conclude once we have shown that there exist at least two bond angles at x that are not equilibrated. In fact, since no acyclic bonds are present in the bond graph and $x \in \mathcal{A}_{\rm bulk}(X_n)$, all the bond angles at x belong to different elementary polygons. Then, there exist at least two non squares in the bond graph and hence $\eta \geq 4$.

It thus remains to prove that there exist $i_1, i_2 \in \{1, \dots, k\}$, $i_1 \neq i_2$, such that $\theta_{i_1}, \theta_{i_2} \notin \{\frac{\pi}{2}, \pi, \frac{3\pi}{2}\}$. Recall $x \in \mathcal{A}(X_n)$. Without restriction we suppose that $\theta_1 \notin \{\frac{\pi}{2}, \pi, \frac{3\pi}{2}\}$. Now assume that $\theta_j \in \{\frac{\pi}{2}, \pi, \frac{3\pi}{2}\}$ for all $j = 2, \dots, k$. Since the bond angles at x need to sum to 2π, we obtain

$$k' \frac{\pi}{2} + \theta_1 = \sum_{i=1}^{k} \theta_i = 2\pi \qquad \text{with} \quad k' = \sum_{j=1}^{3} \#\{i \in \{2, \dots, k\} : \theta_i = j\pi/2\}.$$

By Step 1 we get $\theta_1 \in \frac{\pi}{2}\mathbb{N} \cap [\frac{\pi}{2}, \frac{3\pi}{2}]$. This contradicts the fact that $\theta_1 \notin \{\frac{\pi}{2}, \pi, \frac{3\pi}{2}\}$. □

We are now in the position to prove Theorem 2.3(a).

Proof of Theorem 2.3(a). We prove the statement by induction. For $= 1, 2, 3$ the statement is clearly true, and for $n = 4$ it follows from Lemma 4.2(b). Let $n \geq 5$. By Theorem 2.1 and Lemma 5.8 the bond graph of ground states does not contain bridges and at most one flag. Therefore, in view of Lemma 5.6(ii), up to removing a flag, it is not restrictive to assume that C_n is a ground state with no acyclic bonds. We will use the following fact several times: by Remark 2.2, C_n is repulsion-free. Thus Lemma 5.1 implies

$$\mathcal{R}(C_n^{\rm bulk}) = \mathcal{E}(C_n^{\rm bulk}), \tag{5.11}$$

where $C_n^{\rm bulk}$ is defined before (5.3). By the definition of $\mathcal{A}(X_n)$ and due to the fact that ground states are connected (cf. Theorem 2.1), it suffices to prove that $\mathcal{A}(X_n) = \emptyset$. We divide the proof into two steps. We first prove that $\mathcal{A}(X_n) \setminus \mathcal{A}_{\rm bulk}(X_n) = \emptyset$ and secondly we show that $\mathcal{A}_{\rm bulk}(X_n) = \emptyset$.

Step 1: $\mathcal{A}(X_n) \setminus \mathcal{A}_{\rm bulk}(X_n) = \emptyset$. Assume by contradiction that $\mathcal{A}(X_n) \setminus \mathcal{A}_{\rm bulk}(X_n) \neq \emptyset$. By Lemma 5.3 this implies $\mathcal{R}^{\rm bnd}(C_n) > -2d + 4$. Then (5.11) and Theorem 2.1 (applied for $C_n^{\rm bulk}$) yield

$$\mathcal{R}^{\rm bulk}(C_n) = \mathcal{R}(C_n^{\rm bulk}) = \mathcal{E}(C_n^{\rm bulk}) \geq -\lfloor \beta(n-d) \rfloor.$$

This along with $\mathcal{R}^{\rm bnd}(C_n) > -2d + 4$, (5.3), and again Lemma 5.1 gives

$$\mathcal{E}(C_n) \geq \mathcal{R}(C_n) > -2d + 4 - \lfloor 2(n-d) - 2\sqrt{n-d} \rfloor = -\lfloor 2n - 2\sqrt{n-d} \rfloor + 4. \tag{5.12}$$

By Theorem 2.1, $\mathcal{E}(C_n)$ is an integer and consequently we derive

$$\mathcal{E}(C_n) \geq -\lfloor 2n - 2\sqrt{n-d} \rfloor + 5 \geq -2n + 2\sqrt{n-d} + 5.$$

Now by using Lemma 5.5 and $\mathcal{E}(C_n) = -b$ (see Theorem 2.1) we obtain

$$\mathcal{E}(C_n) \geq -2n + 2\sqrt{-2\mathcal{E}(C_n) + 4 - 3n + \eta} + 5.$$

Observe that $\eta \geq 2$ by Lemma 5.9. By applying Lemma 5.7 with $j = 5, m = \eta$ and $x = \mathcal{E}(C_n)$ we conclude $\mathcal{E}(C_n) \geq -\beta(n) + 1 > -\lfloor \beta(n) \rfloor$. This contradicts Theorem 2.1.

Step 2: $\mathcal{A}_{\rm bulk}(X_n) = \emptyset$. Assume by contradiction that $\mathcal{A}_{\rm bulk}(X_n) \neq \emptyset$. Note that $\eta \geq 4$ by Lemma 5.9 and thus $n \geq 8$. There are two cases two consider: a) $n - d \leq 3$ and b) $n - d \geq 4$.

Proof for $n - d \leq 3$. Using Lemma 5.5 we have that

$$2b + 4 - 3n + \eta = n - d \leq 3. \tag{5.13}$$

By Theorem 2.1 we have that $\mathcal{E}(C_n) = -b = -\lfloor 2n - 2\sqrt{n}\rfloor$. This together with (5.13) leads to

$$-2n - \lfloor -2\sqrt{n}\rfloor = -\lfloor 2n - 2\sqrt{n}\rfloor = \mathcal{E}(C_n) \geq -\frac{3}{2}n + \frac{1}{2}(1+\eta) \geq -\frac{3}{2}n + \frac{5}{2}, \tag{5.14}$$

where the last step follows from $\eta \geq 4$. Inequality (5.14) is violated for all $n \geq 8$. This yields a contradiction and concludes the proof in this case.

Proof for $n - d \geq 4$. First, assume that the bond graph of C_n^{bulk} does not contain a flag. By induction hypothesis, ground states with less than n atoms without flags are subsets of the square lattice. Thus, by the assumption $\mathcal{A}_{\mathrm{bulk}}(X_n) \neq \emptyset$, C_n^{bulk} cannot be a ground state. This along with (5.3) and (5.11) yields

$$\mathcal{R}^{\mathrm{bulk}}(C_n) = \mathcal{R}(C_n^{\mathrm{bulk}}) = \mathcal{E}(C_n^{\mathrm{bulk}}) > -\lfloor \beta(n-d)\rfloor. \tag{5.15}$$

By Lemma 5.3 we also have $\mathcal{R}^{\mathrm{bnd}}(C_n) \geq -2d + 4$. The two inequalities together with (5.3) lead to the strict inequality (5.12), and we may proceed exactly as in Step 1 of the proof to obtain a contradiction to the fact that C_n is a ground state.

Now assume that the bond graph of C_n^{bulk} contains a flag. Without restriction we can assume that C_n^{bulk} is a ground state since otherwise the strict inequality (5.15) holds, and we obtain a contradiction exactly as before. Since $n-d \geq 4$, the bond graph of C_n^{bulk} contains exactly one flag by Lemma 5.8. There holds $\#\mathcal{A}(X_n) \geq 2$ by Lemma 5.9 and $\mathcal{A}(X_n) \setminus \mathcal{A}_{\mathrm{bulk}}(X_n) = \emptyset$ by Step 1. Therefore, $\#\mathcal{A}_{\mathrm{bulk}}(X_n) \geq 2$. After removing the flag from C_n^{bulk}, we get a configuration C_{n-d-1} which does not contain flags, but there still holds $\mathcal{A}(X_n) \cap X_{n-d-1} \neq \emptyset$. By induction hypothesis, C_{n-d-1} can thus not be a ground state and we get $\mathcal{E}(C_{n-d-1}) > -\lfloor \beta(n-d-1)\rfloor$. By counting the contribution of the flag to the energy by at least -1 we obtain

$$\mathcal{R}(C_n^{\mathrm{bulk}}) = \mathcal{E}(C_n^{\mathrm{bulk}}) > -1 - \lfloor \beta(n-d-1)\rfloor,$$

where we also used (5.11). This along with $\mathcal{R}^{\mathrm{bnd}}(C_n) \geq -2d+4$ (see Lemma 5.3) and (5.3) gives

$$\mathcal{E}(C_n) > -1 - 2d + 4 - \lfloor \beta(n-d-1)\rfloor = -\lfloor 2n - 2\sqrt{n-d-1}\rfloor + 5.$$

Since $\mathcal{E}(C_n) = -b$ is an integer by Theorem 2.1, we obtain $\mathcal{E}(C_n) \geq -2n + 6 + 2\sqrt{n-d-1}$. Now using Lemma 5.5 and $\mathcal{E}(C_n) = -b$ we obtain

$$\mathcal{E}(C_n) \geq -2n + 6 + 2\sqrt{-2\mathcal{E}(C_n) + 3 - 3n + \eta}.$$

Recall that $\eta \geq 4$ by Lemma 5.9. By applying Lemma 5.7 with $j = 6, m = \eta - 1$ and $x = \mathcal{E}(C_n)$ we obtain

$$\begin{aligned}\mathcal{E}(C_n) &\geq -2n + 2\sqrt{\eta + n - 5} + 2 \geq -2n + 2\sqrt{n-1} + 2 \\ &= -2n + 2\sqrt{n} - 2\sqrt{n} + 2\sqrt{n-1} + 2 = -2n + 2\sqrt{n} + 2 - \frac{2}{\sqrt{n} + \sqrt{n-1}}.\end{aligned}$$

Recall that $n \geq 8$. Therefore, we get $2 - \frac{2}{\sqrt{n}+\sqrt{n-1}} \geq 1$ and thus

$$\mathcal{E}(C_n) \geq -2n + 2\sqrt{n} + 1 > -\lfloor 2n - 2\sqrt{n}\rfloor.$$

This contradicts the fact that C_n is a ground state and concludes the proof. □

We now address the proof of Theorem 2.3(b). To this end, we use the following result.

Theorem 5.10 (Deviation from Wulff-shape)**.** *Let $n \in \mathbb{N}$ and let C_n be a ground state with no acyclic bonds. Then, possibly after translation we find two squares $S_{k_1^2} \subset \mathbb{Z}^2$ and $S_{k_2^2} \subset \mathbb{Z}^2$, $k_1, k_2 \in \mathbb{N}$, with $S_{k_1^2} \subset X_n \subset S_{k_2^2}$ such that*

$$0 < k_2 - k_1 \leq cn^{\frac{1}{4}},$$

where $c > 0$ is a universal constant independent of n and C_n.

Proof. Let $n \geq 4$. From Theorem 2.3(a) and the fact that C_n does not contain acyclic bonds we get that C_n is a subset of the square lattice. Moreover, C_n is repulsion-free, see Remark 2.2. Therefore, our energy on ground-state configurations coincides (up to distributing alternating charge or neglecting it) with the one considered in [23]. The statement then follows from [23, Theorem 8.1]. □

Proof of Theorem 2.3(b). By Theorem 2.1 and Lemma 5.8 we know that the bond graph contains at most one flag and no other acyclic bonds. If it contains a flag, one can remove the flag and the remaining configuration is still a ground state by Lemma 5.6(i). We can therefore assume that there are no acyclic bonds in the bond graph of C_n. The statement follows from Theorem 5.10. In fact, observe that Theorem 5.10 also implies that the diameter of a ground state is of order $\sqrt{n}$. □

5.4. **Characterization of the net charge.** We now prove Theorem 2.4. Part (b) of the statement has already been addressed by an explicit construction in Subsection 3.2. Thus, it remains to prove part (i).

Definition 5.11 (Line segment)**.** A tuple $(x_0, \dots, x_m) \subset \mathbb{Z}^2$ is called a *line segment* if there exists $v \in \{(1,0),(0,1)\}$ such that $x_{k+1} = x_k + v$ for all $k \in \{0, \dots, m-1\}$.

Proposition 5.12 (Convexity of ground states)**.** *Let $n \in \mathbb{N}$ and let C_n be a ground state with no acyclic bonds. Then each line segment $(x_0, \dots, x_m)$ with $x_0, x_m \in X_n$ satisfies $x_i \in X_n$ for $i = 0, \dots, m$.*

Proof. For the proof we refer to [23, Proposition 6.3], where this property is called *convexity by rows and columns*. The result in [23, Proposition 6.3] is applicable due to the fact that our energy on ground-state configurations coincides with the one considered in [23], see the proof of Theorem 5.10. □

Proof of Theorem 2.4(a). In view of Theorem 2.1 and Lemma 5.8, it suffices to treat the case that the bond graph of C_n does not contain any acyclic bonds. We apply Theorem 5.10 to find two squares $S_{k_1^2} \subset X_n \subset S_{k_2^2}$. By Proposition 5.12 it is elementary to see that $X_n \setminus S_{k_1^2}$ can be written as the union of at most $4(k_2 - k_1)$ line segments. Recall that C_n has alternating charge distribution and therefore the net charge of each line segment is in $\{-1, 0, 1\}$. Also recall from Subsection 3.1 that squares have charge in $\{-1, 0, 1\}$. This implies that the net charge of the configuration C_n satisfies

$$|\mathcal{Q}(C_n)| \le 4(k_2 - k_1) + 1.$$

The statement follows from the fact that $k_2 - k_1 \le cn^{1/4}$, see Theorem 5.10. □

6. Characterization of optimal configurations for Prescribed charge

In this section we prove Proposition 2.5, Theorem 2.6, and Theorem 2.8.

6.1. **Energy of optimal configurations.** In this short subsection we prove Theorem 2.6.

Proof of Theorem 2.6: Without restriction we may suppose that $q_{\rm net} \ge 0$ since the proof for $q_{\rm net} \le 0$ follows analogously. We proceed in two steps. First, we prove the statement for $q_{\rm net} \ge q^n_{\rm sat}$ and then for $0 \le q_{\rm net} < q^n_{\rm sat}$. The proof is performed by an induction argument.

Step 1: $q_{\rm net} \ge q^n_{\rm sat}$. Our goal is to show

$$\mathcal{E}^n_{\rm min}(q_{\rm net}) = -2n + 2q_{\rm net} \quad \text{for all} \quad q_{\rm net} \ge q^n_{\rm sat}. \tag{6.1}$$

For $q_{\rm net} = q^n_{\rm sat}$ the statement is clearly true, see (2.12). Suppose that the statement holds for $q_{\rm net} \ge q^n_{\rm sat}$ with $q_{\rm net} \le n - 2$. We show (6.1) for $q_{\rm net} + 2$. By Lemma 4.3(a), for all configurations C_n satisfying $\mathcal{Q}(C_n) = q_{\rm net} + 2$ there holds $\mathcal{E}(C_n) \ge -2n + 2(q_{\rm net} + 2)$.

It thus suffices to construct a configuration $\tilde{C}_n$ with $\mathcal{Q}(\tilde{C}_n) = q_{\rm net} + 2$ and $\mathcal{E}(\tilde{C}_n) = -2n + 2(q_{\rm net} + 2)$. To this end, let C_n be a configuration with $\mathcal{Q}(C_n) = q_{\rm net}$ and $\mathcal{E}(C_n) = -2n + 2q_{\rm net}$, which exists by the induction hypothesis.

Choose $x_i \in C_n$ with $q_i = -1$ and modify C_n as follows: remove x_i and add a new atom $\tilde{x}_i$ with charge $+1$ to the configuration such that $|\tilde{x}_i - x_j| \ge \sqrt{2}$ for all $j = 1, \dots, n$. Denote this configuration by $\tilde{C}_n$. We have $\mathcal{Q}(\tilde{C}_n) = q_{\rm net} + 2$. By Lemma 4.3(a)(i), the relocated atom was 4-bonded and the bond lengths were of unit length. Hence, we obtain by [ii]

$$\mathcal{E}(\tilde{C}_n) = \mathcal{E}(C_n) + 4 = -2n + 2q_{\rm net} + 4 = -2n + 2(q_{\rm net} + 2).$$

Thus, (6.1) is proven for $q_{\rm net} + 2$.

Step 2: $0 \le q_{\rm net} < q^n_{\rm sat}$. As before, the lower bound in (2.14) follows from Lemma 4.3(a). Therefore, it remains to show that

$$\mathcal{E}^n_{\min}(q_{\rm net}) \le -2n + 4q^n_{\rm sat} - 2q_{\rm net} \quad \text{ for all } 0 \le q_{\rm net} \le q^n_{\rm sat}. \tag{6.2}$$

For $q_{\rm net} = q^n_{\rm sat}$ the statement is clearly true. Assume that (6.2) holds for $2 \le q_{\rm net} \le q^n_{\rm sat}$. We show (6.2) for $q_{\rm net} - 2$. To this end, we have to construct a configuration $\tilde{C}_n$ with $\mathcal{Q}(\tilde{C}_n) = q_{\rm net} - 2$ and $\mathcal{E}(\tilde{C}_n) \le -2n + 4q^n_{\rm sat} - 2(q_{\rm net} - 2)$.

Let C_n be a configuration with $\mathcal{Q}(C_n) = q_{\rm net}$ and $\mathcal{E}(C_n) = \mathcal{E}^n_{\min}(q_{\rm net})$. Choose an atom x_i with $q_i = 1$ and modify C_n in the following way: remove x_i and add a new atom $\tilde{x}_i$ with charge -1 to the configuration such that $|\tilde{x}_i - x_j| \ge \sqrt{2}$ for all $j = 1, \dots, n$. Denote this configuration by $\tilde{C}_n$. First, note that $\mathcal{Q}(\tilde{C}_n) = q_{\rm net} - 2$. By [ii] and $\#\mathcal{N}(x_i) \le 4$, see Lemma 4.1, we get

$$\mathcal{E}(\tilde{C}_n) \le \mathcal{E}(C_n) + 4.$$

As (6.2) holds for $q_{\rm net}$ by induction hypothesis, we obtain

$$\mathcal{E}^n_{\min}(q_{\rm net} - 2) \le \mathcal{E}(\tilde{C}_n) \le \mathcal{E}(C_n) + 4 \le -2n + 4q^n_{\rm sat} - 2q_{\rm net} + 4 = -2n + 4q^n_{\rm sat} - 2(q_{\rm net} - 2).$$

This shows (6.2) for $q_{\rm net} - 2$ and concludes the proof. □

6.2. **Boundary and interior net charge.** In the following, we will consider without restriction configurations which satisfy $\mathcal{Q}(C_n) \ge 0$, i.e., the $+1$ phase is the majority phase. This can indeed always be achieved by interchanging the roles of the positive and negative charges. We define the notion of a bridging atom. An atom x_0 is called *bridging atom* if it is 2-bonded and not contained in any simple cycle, see Fig. 11. Denote by C_m and C_{n-m-1} the two connected components of $C_n \setminus \{x_0, q_0\}$. We set

$$C_{m+1} = C_m \cup \{(x_0, q_0)\}, \quad C_{n-m} = C_{n-m-1} \cup \{(x_0, q_0)\}. \tag{6.3}$$

In the following we say that C_m and C_{m-n} are *connected through a bridging atom*. Recall the definition of acyclic bonds in Subsection 2.2. In a similar fashion, we say that an atom x_i is an *acyclic atom* if it is not contained in any cycle. We denote the union of the acyclic atoms by $I_{\rm ac}$.

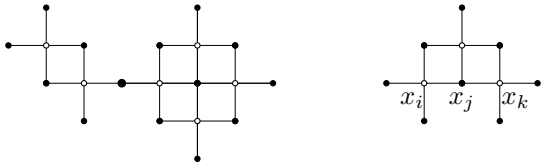

FIGURE 11. On the left: A configuration with a bridging atom illustrated bold. On the right: A configuration with $I_{\rm ac} \cap X^-_n = \emptyset$, where the atoms X^-_n defined in (2.6) are illustrated in white.

Lemma 6.1 (Bridging atom)**.** *Consider C_n with $0 \le \mathcal{Q}(C_n)$ and $\mathcal{E}(C_n) = -2n + 2\mathcal{Q}(C_n)$.*

(a) If there exists a bridging atom connecting two configurations C_m and C_{n-m}, there holds

$$\mathcal{Q}(C_m) \ge q^{m+1}_{\rm sat} - 1 \quad \text{ and } \quad \mathcal{Q}(C_{n-m}) \ge q^{n-m}_{\rm sat}.$$

Moreover, C_{n-m} is an optimal configuration.

(b) If $n \ge 6$ and C_n is connected without bridging atoms, then $I_{\rm ac} \cap X^-_n = \emptyset$ and $I_{\rm ac} \cap X^+_n$ consists of 1-bonded atoms.

Proof. (a) Suppose that a bridging atom x_0 exists. As $\mathcal{E}(C_n) = -2n + 2\mathcal{Q}(C_n)$, Lemma 4.3(a)(i) implies that x_0 has charge $q_0 = +1$. This clearly gives

$$\mathcal{Q}(C_{m+1}) = \mathcal{Q}(C_m) + 1. \tag{6.4}$$

Define by C_{n+1} a configuration given by the union of the two connected components C_{n-m} and C_{m+1}, where C_{m+1} is translated in such a way that $\operatorname{dist}(X_{n-m}, X_{m+1}) \ge \sqrt{2}$. We observe that the atoms of

charge -1 are 4-bonded by construction since C_n satisfies this property. In a similar fashion, C_{n+1} is repulsion-free and its bonds have unit length by Lemma 4.3(a)(i),(ii). Therefore, in view of Lemma 4.3(b), for C_{n+1} there holds the equality $\mathcal{E}(C_{n+1}) = -2(n+1) + 2\mathcal{Q}(C_{n+1})$. Then applying Lemma 4.3(a)(vi) on the two connected components C_{m+1} and C_{n-m} we find $\mathcal{Q}(C_{m+1}) \geq q_{\rm sat}^{m+1}$ and $\mathcal{Q}(C_{n-m}) \geq q_{\rm sat}^{n-m}$. The first part of the claim now follows from (6.4).

In view of Lemma 4.3(b), for C_{n-m} there holds the equality $\mathcal{E}(C_{n-m}) = -2(n-m) + 2\mathcal{Q}(C_{n-m})$. Thus, C_{n-m} is an optimal configuration by (4.5).

(b) Now assume that $n \geq 6$ and that C_n is connected without bridging atoms. First, suppose by contradiction that there exists some $x_i \in I_{\rm ac} \cap X_n^- \neq \emptyset$. Since C_n is connected with alternating charge distribution (see (4.5) and Lemma 4.1) and $n \geq 6$, there exist $x_k \in X_n^-$, $x_k \neq x_i$, and $x_j \in \mathcal{N}(x_i) \cap \mathcal{N}(x_k)$. Since C_n does not contain bridging atoms and $x_i \in I_{\rm ac}$, x_j is at least 3-bonded. By Lemma 4.3(a)(iv),(v) all bond angles of x_j are integer multiples of $\frac{\pi}{2}$. Thus, as sketched in Fig. 11, x_i is contained in a square. This contradicts $x_i \in I_{\rm ac}$. In a similar fashion, Fig. 11 shows that some $x_j \in X_n^+$ which is 3-bonded or 4-bonded is contained in a square. This along with (4.1) and the fact that by assumption there are no 2-bonded atoms in $I_{\rm ac}$, shows that $I_{\rm ac} \cap X_n^+$ consists of 1-bonded atoms only. □

Sub-configurations: Similar to the definition of $I_{\rm ac}$, we say that an atom x_i is an *exterior acyclic atom* if it is not contained in any cycle and not contained in the interior region of any cycle. We denote the union of the exterior acyclic atoms by $I_{\rm ac}^{\rm ext}$. Clearly, there holds $I_{\rm ac}^{\rm ext} \subset I_{\rm ac}$.

Let $n \geq 6$ and let C_n be a connected, optimal configuration without bridging atoms satisfying $\mathcal{Q}(C_n) \geq q_{\rm sat}^n$. In particular, there holds $\mathcal{E}(C_n) = -2n + 2\mathcal{Q}(C_n)$ by Theorem 2.6. We denote by C_n^a the configuration without the exterior acyclic atoms and their charges. We observe that C_n^a is still connected. This follows from Lemma 6.1(b). By ∂C_n^a we indicate the maximal polygon of C_n^a, i.e, the simple cycle which delimits the bond graph, see also Subsection 5.1. The cardinality of ∂C_n^a is denoted by d. Furthermore, for $k = 2, 3, 4$, we set

$$I_k = \{x_i \in \partial X_n^a : \quad \#(\mathcal{N}(x_i) \cap X_n^a) = k\}. \tag{6.5}$$

Finally, we set $C_n^{a,\rm bulk} = C_n^a \setminus \partial C_n^a$. In a similar fashion, we denote by X_n^a, ∂X_n^a, and $X_n^{a,\rm bulk}$ the atomic positions of the sub-configurations. Recall the definition of η in (2.3).

Lemma 6.2 (Cardinality of $n-d$)**.** *Let $n \geq 6$ and let C_n be a connected, optimal configuration which satisfies $\mathcal{Q}(C_n) \geq q_{\rm sat}^n$ and does not contain a bridging atom. Then*

$$n - d \in n + 4 - 4\mathcal{Q}(C_n) + \eta + 2\#I_{\rm ac}^{\rm ext} + 2\mathbb{N}_0.$$

Proof. Let f_j be the number elementary j-gons in the bond graph and let f be the number of elementary polygons. There holds

$$\sum_{j \geq 4} j f_j = 2b - d - 2b_{\rm ac},$$

where $b_{\rm ac}$ denotes the cardinality of the acyclic bonds. In fact, by the summation on the left the bonds of the maximal polygon are counted once, the acyclic bonds are not counted, and all other bonds are counted twice. By Lemma 4.2(a) we obtain $4f + \eta = 2b - d - 2b_{\rm ac}$. This along with Euler's formula $n - b + f = 1$ (omitting the exterior face) and the fact that $b_{\rm ac} \geq \#I_{\rm ac}^{\rm ext}$ yields

$$n - d \in 2b + 4 - 3n + \eta + 2\#I_{\rm ac}^{\rm ext} + 2\mathbb{N}_0.$$

As $b = 2n - 2\mathcal{Q}(C_n)$, see Remark 2.2, Theorem 2.6, and Lemma 4.3(a)(i),(ii), the claim follows. □

Recall the definition of the non-equilibrated atoms $\mathcal{A}(X_n)$ in Subsection 2.2. The following estimate for the net charge of the boundary and the interior configuration will be instrumental for our analysis. Its proof will be given in Appendix A, along with the proof of the boundary energy estimate (Lemma 5.3).

Lemma 6.3 (Net charge of the interior and boundary)**.** *Let $n \geq 6$ and let C_n be a connected q^n_{sat}-optimal configuration without bridging atoms.*

(a) Then there exists $m \geq 4$ such that

$$\#I_2 + 2\#I_3 + 3\#I_4 = 2d - m. \tag{6.6}$$

If $\#\mathcal{A}(X_n) \geq \#\mathcal{A}(X_n^{\mathrm{a,bulk}}) + 2$, then $m \geq 6$.

(b) Suppose that (6.6) holds. Then $\#I_{\mathrm{ac}}^{\mathrm{ext}} \geq m$ and there exists an optimal configuration C_{n-d-m} satisfying $\mathcal{Q}(C_{n-d-m}) \geq q_{\mathrm{sat}}^{n-d-m}$ and

$$\mathcal{Q}(C_n) = \mathcal{Q}(C_{n-d-m}) + m. \tag{6.7}$$

Moreover, X_{n-d-m} is a subset of X_n up to 0-bonded atoms and $\mathcal{A}(X_{n-d-m}) = \mathcal{A}(X_n^{\mathrm{a,bulk}})$.

Roughly speaking, the configurations C_{n-d-m} are constructed by removing ∂X_n^a and $I_{\mathrm{ac}}^{\mathrm{ext}}$ from C_n. In this sense, $\mathcal{Q}(C_{n-d-m})$ can be regarded as the net charge of the interior. The statement then shows that the boundary net charge can be controlled from below by 4, and by at least 6 if the number of non-equilibrated atoms decreases by at least 2 when the boundary is removed.

6.3. **Characterization of q^n_{sat}.** The goal of this subsection is to prove Proposition 2.5. In view of the construction in Subsection 3.3, see Proposition 3.2, it remains to show the lower bound $q^n_{\mathrm{sat}} \geq \phi(n)$, where the function ϕ is defined in (2.13). As a preparation, we first provide an equivalent representation of ϕ, and state some monotonicity and subadditivity properties.

Lemma 6.4 (Representation of ϕ)**.** *For $n \geq 2$ there holds*

$$\phi(n) = \begin{cases} 2 + 2k + 0 & \text{if } n = 1 + 2k^2 + 2k + m, \quad 1 \leq m \leq 2k+2, \ m \text{ odd}, \\ 2 + 2k + 1 & \text{if } n = 1 + 2k^2 + 2k + m, \quad 1 \leq m \leq 2k+2, \ m \text{ even}, \\ 3 + 2k + 1 & \text{if } n = 1 + 2k^2 + 2k + m, \quad 2k+3 \leq m \leq 4k+4, \ m \text{ odd}, \\ 3 + 2k + 0 & \text{if } n = 1 + 2k^2 + 2k + m, \quad 2k+3 \leq m \leq 4k+4, \ m \text{ even}, \end{cases} \tag{6.8}$$

where $k \in \mathbb{N}_0$.

Proof. We divide the proof into two steps. First, we prove the statement in the case that n is even and then in the case that n is odd.

n even. Let $n = 1 + 2k^2 + 2k + m$ with n even, i.e., $1 \leq m \leq 4k+4$ and m odd. By (2.13) we have

$$\phi(n) = 2 + 2\lfloor \tfrac{1}{2}\sqrt{2n-4} \rfloor = 2 + 2\lfloor \tfrac{1}{2}\sqrt{4k^2 + 4k + 2m - 2} \rfloor. \tag{6.9}$$

It is elementary to check that

$$\lfloor \tfrac{1}{2}\sqrt{4k^2 + 4k + 2m - 2} \rfloor = k \qquad \text{for all } 1 \leq m \leq 2k+2, \ m \text{ odd},$$
$$\lfloor \tfrac{1}{2}\sqrt{4k^2 + 4k + 2m - 2} \rfloor = k+1 \qquad \text{for all } 2k+3 \leq m \leq 4k+4, \ m \text{ odd}.$$

This along with (6.9) shows the desired equality of $\phi(n)$ with the expression on the right hand side of (6.8), in the case that n is even.

n odd. Let $n = 1 + 2k^2 + 2k + m$ with n odd, i.e., $1 \leq m \leq 4k+4$ and m even. By (2.13) we have

$$\phi(n) = 3 + 2\lfloor -\tfrac{1}{2} + \tfrac{1}{2}\sqrt{2n-5} \rfloor = 3 + 2\lfloor -\tfrac{1}{2} + \tfrac{1}{2}\sqrt{4k^2 + 4k + 2m - 3} \rfloor. \tag{6.10}$$

It is again elementary to see that

$$\lfloor -\tfrac{1}{2} + \tfrac{1}{2}\sqrt{4k^2 + 4k + 2m - 3} \rfloor = k \qquad \text{for all } 1 \leq m \leq 4k+4, \ m \text{ even}.$$

This together with (6.10) shows the desired equality of $\phi(n)$ with the expression on the right hand side of (6.8), in the case that n is odd. □

Lemma 6.5 (Properties of ϕ)**.** *The following properties hold true*

(i) $\phi(n) \leq \phi(n-1) + 1$ *and* $\phi(n) \leq \phi(n+1) + 1$ *for all* $n \in \mathbb{N}$,

(ii) $\phi(n) \le \phi(n+2)$ *for all* $n \in \mathbb{N}$,
(iii) $\phi(n) \le \phi(n-3)+1$ *for all* $n \ge 5$,
(iv) $\phi(n) \le \phi(n-5)+1$ *for all* $n \ge 11$,
(v) $\phi(n_1-t)+\phi(n_2+t) \le \phi(n_1)+\phi(n_2)+6$ *for all* $t \le n_1 \le n_2$.
(vi) $\phi(n)+2 \le \phi(m)+\phi(n-m)$ *for all* $3 \le m, n-m \le n, \quad n \ge 11$,
(vii) *There exists* $m_0 \in \mathbb{N}$ *such that* $\phi(n)+52 \le \phi(m)+\phi(n-m)$ *for all* $m_0 \le m, n-m \le n$.

Proof. Properties (i)-(v) are elementary and can be checked by using (6.8): for (ii), we use the monotonicity of ϕ when restricted to even and odd numbers, respectively. Property (i) follows by looking closely at (6.8). To see (iii)-(iv), we denote by $k(n) \in \mathbb{N}_0$ and $1 \le m(n) \le 4k(n)+4$ the numbers such that $n = 1+2(k(n))^2+2k(n)+m(n)$. We also set $n_3 = 7$ and $n_5 = 15$. It is elementary to check that for $t \in \{3,5\}$ and for all $n \ge n_t$ there holds either $k(n) = k(n-t)$ or

$$k(n) = k(n-t)+1, \qquad m(n) \le 2k(n)+2, \qquad m(n-t) \ge 2k(n-t)+3.$$

This along with a careful inspection of (6.8) implies (iii)-(iv) for $n \ge 7$ and $n \ge 15$ respectively. The remaining cases can be checked by Table 1. To see (v), we first note that for $0 \le m \le n$ there holds $\phi(n)-\phi(m) \le 2(k(n)-k(m))+2$ and $\phi(m)-\phi(n) \le 2(k(m)-k(n))+2$. This can be seen by careful inspection of (6.8). Additionally, we use that for $t \le n_1 \le n_2$ there holds $k(n_1-t)-k(n_1)+k(n_2+t)-k(n_2) \le 1$.

We proceed with (vi). The case $m = 3$ follows from (iii) and $\phi(3) = 3$, see Table 1 below. The case $m = 4$ follows by taking additionally (i) and $\phi(4) = 4$ into account. For $m = 5$, we use (iv) and the fact that $\phi(5) = 3$. Now suppose that $n \ge 11$ and $6 \le m, n-m \le n$.

We will use the following property: let $k_1, k_2, m_0 \in \mathbb{N}$, with $m_0 \ge k_1 \ge k_2$. Since the function $x \mapsto \sqrt{x}$ is concave and increasing, the function

$$m \mapsto \frac{1}{2}\sqrt{2m-k_1}+\frac{1}{2}\sqrt{2(n-m)-k_2}, \quad m_0 \le m, n-m \le n \tag{6.11}$$

attains its minimum for $m = m_0$. Moreover, we will use that $\lfloor a+b \rfloor \le \lfloor a \rfloor + \lfloor b \rfloor + 1$. We will work directly with the definition of ϕ, see (2.13). Consulting Table 1, we note that the cases $11 \le n \le 32$ can be checked directly by comparing the values of $\phi(n-m)+\phi(m)$ and $\phi(n)$. We can therefore assume that $n \ge 33$. There are four cases to consider: (a) n even, m even. (b) n even, m odd. (c) n odd, m even. (d) n odd, m odd.

(a) n even, m even. By (6.11) for $k_1 = k_2 = 4$ and $m_0 = 6$, we get

$$\begin{aligned}
\phi(m)+\phi(n-m) &= 2\lfloor \tfrac{1}{2}\sqrt{2m-4} \rfloor + 2\lfloor \tfrac{1}{2}\sqrt{2(n-m)-4} \rfloor + 4 \\
&\ge 2\lfloor \tfrac{1}{2}\sqrt{2m-4}+\tfrac{1}{2}\sqrt{2(n-m)-4} \rfloor + 2 \\
&\ge 2\lfloor \tfrac{1}{2}\sqrt{8}+\tfrac{1}{2}\sqrt{2n-16} \rfloor + 2 \\
&= 2\left\lfloor \frac{1}{2}\sqrt{2n-4}+\sqrt{2}-\frac{6}{\sqrt{2n-4}+\sqrt{2n-16}} \right\rfloor + 2.
\end{aligned}$$

Now for $n \ge 32$ we have that $\sqrt{2}-6(\sqrt{2n-4}+\sqrt{2n-16})^{-1} \ge 1$, which indeed yields $\phi(m)+\phi(n-m) \ge 2\lfloor \frac{1}{2}\sqrt{2n-4} \rfloor + 2 + 2 = \phi(n)+2$.

(b) n even, m odd. Observe that in this case we have $m, n-m \ge 7$ and thus $n \ge 14$. By (6.11) for $k_1 = k_2 = 5$ and $m_0 = 7$, we obtain

$$\begin{aligned}
\phi(m)+\phi(n-m) &= 2\lfloor -\tfrac{1}{2}+\tfrac{1}{2}\sqrt{2m-5} \rfloor + 2\lfloor -\tfrac{1}{2}+\tfrac{1}{2}\sqrt{2(n-m)-5} \rfloor + 6 \\
&\ge 2\lfloor \tfrac{1}{2}\sqrt{2m-5}+\tfrac{1}{2}\sqrt{2(n-m)-5}-1 \rfloor + 4 \\
&\ge 2\lfloor \tfrac{1}{2}\sqrt{9}+\tfrac{1}{2}\sqrt{2n-19}-1 \rfloor + 4 \\
&= 2\left\lfloor \frac{1}{2}\sqrt{2n-4}+\frac{1}{2}-\frac{1}{2}\frac{15}{\sqrt{2n-4}+\sqrt{2n-19}} \right\rfloor + 4.
\end{aligned}$$

We check that for all $n \geq 34$ (note n is even) there holds $1 - 15(\sqrt{2n-4} + \sqrt{2n-19})^{-1} \geq 0$, and thus $\phi(m) + \phi(n-m) \geq \phi(n) + 2$.

(c) n odd, m even. By (6.11) for $k_1 = 5$, $k_2 = 4$ and $m_0 = 6$, we obtain

$$\begin{aligned}\phi(m) + \phi(n-m) &= 2\lfloor \tfrac{1}{2}\sqrt{2m-4} \rfloor + 2\lfloor -\tfrac{1}{2} + \tfrac{1}{2}\sqrt{2(n-m)-5} \rfloor + 5 \\ &\geq 2\lfloor \tfrac{1}{2}\sqrt{2m-4} + \tfrac{1}{2}\sqrt{2(n-m)-5} - \tfrac{1}{2} \rfloor + 3 \\ &\geq 2\lfloor \tfrac{1}{2}\sqrt{8} + \tfrac{1}{2}\sqrt{2n-17} - \tfrac{1}{2} \rfloor + 3 \\ &= 2\left\lfloor \frac{1}{2}\sqrt{2n-5} - \frac{1}{2} + \sqrt{2} - \frac{6}{\sqrt{2n-5} + \sqrt{2n-17}} \right\rfloor + 3.\end{aligned}$$

For $n \geq 33$ we have that $\sqrt{2} - 6(\sqrt{2n-5} + \sqrt{2n-17})^{-1} \geq 1$.

(d) n odd, m odd. We proceed as in (c) by interchanging the roles of m and $n-m$.

Finally, to see (vii), one may follow the lines of the proof of (vi). We sketch only the case where n and m are even. By repeating the argument in (a) for general m_0 we find

$$\phi(m) + \phi(n-m) \geq 2\left\lfloor \frac{1}{2}\sqrt{2n-4} + \tfrac{1}{2}\sqrt{2m_0-4} - \frac{m_0}{\sqrt{2n-4} + \sqrt{2n-2m_0-4}} \right\rfloor + 2.$$

One can check that for $m_0 = 3945$ we have $\phi(m) + \phi(n-m) \geq \phi(n) + 52$ for all $n \geq 2m_0$. □

n	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
$\phi(n)$	1	2	3	4	3	4	5	4	5	6	5	6	5	6	7	6
n	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32
$\phi(n)$	7	6	7	8	7	8	7	8	7	8	9	8	9	8	9	8

TABLE 1. The function $\phi(n)$ for $1 \leq n \leq 32$.

We now are in a position to establish the lower bound for q^n_{sat}. This lower bound together with the upper bound in Proposition 3.2 shows Proposition 2.5.

Proposition 6.6 (Lower bound for q^n_{sat})**.** *Let $n \in \mathbb{N}$. Then $q^n_{\mathrm{sat}} \geq \phi(n)$.*

Proof. Let C_n be a q^n_{sat}-optimal configuration, i.e., $\mathcal{Q}(C_n) = q^n_{\mathrm{sat}}$ and $\mathcal{E}(C_n) = \mathcal{E}^n_{\min}(q^n_{\mathrm{sat}}) = -2n + 2q^n_{\mathrm{sat}}$. We proceed to show that $q^n_{\mathrm{sat}} = \mathcal{Q}(C_n) \geq \phi(n)$. We prove the claim by induction. In view of Table 1, it is elementary to check that for $1 \leq n \leq 10$ the claim holds. Indeed, for $1 \leq n \leq 4$ the cardinality of the minority phase is zero, for $5 \leq n \leq 7$ the cardinality of the minority phase is at most one, and for $8 \leq n \leq 10$ the cardinality of the minority phase is at most two. This is due to the fact that by Lemma 4.3(a)(i),(iv) each atom of the minority phase is 4-bonded with bond angles $\pi/2$ and thus two atoms of the minority phase can share at most two neighbors. Finally, three such atoms can only have one neighbor in common.

Let $n \geq 11$. We assume that the statement holds for all $m \in \mathbb{N}$ with $1 \leq m < n$, and prove the statement for n. We proceed in three steps. First, we show that the claim holds true if C_n is not connected. Then, we treat the case where C_n is connected and contains a bridging atom. Finally, we address the case of connected C_n without any bridging atoms.

Step 1: C_n is not connected. We assume that C_n is not connected. Denote by C_m and C_{n-m}, $1 \leq m, n-m \leq n$, two sub-configurations consisting of m and $n-m$ atoms, respectively, with no bonds between them. Lemma 4.3(a)(vi) implies that $\mathcal{Q}(C_m) \geq q^m_{\mathrm{sat}}$ and $\mathcal{Q}(C_{n-m}) \geq q^{n-m}_{\mathrm{sat}}$. Suppose that $m \leq 2$ or $n - m \leq 2$, without restriction say $m \leq 2$. We can apply the induction hypothesis, Table 1, and Lemma 6.5(i) (m times) to obtain

$$\mathcal{Q}(C_n) = \mathcal{Q}(C_m) + \mathcal{Q}(C_{n-m}) \geq q^m_{\mathrm{sat}} + q^{n-m}_{\mathrm{sat}} \geq \phi(m) + \phi(n-m) = m + \phi(n-m) \geq \phi(n).$$

On the other hand, if $m, n-m \geq 3$, the induction hypothesis and Lemma 6.5(vi) (recall $n \geq 11$) yield

$$q^n_{\rm sat} = \mathcal{Q}(C_n) = \mathcal{Q}(C_m) + \mathcal{Q}(C_{n-m}) \geq \phi(m) + \phi(n-m) \geq 2 + \phi(n).$$

This yields the claim in the case that C_n is not connected.

Step 2: C_n is connected and contains bridging atoms. Assume that the bond graph contains a bridging atom. Denote the two configurations that a connected through a bridging atom by C_m and C_{n-m}, see the definition before (6.3). By Lemma 6.1(a) and the induction hypothesis we have

$$\mathcal{Q}(C_m) \geq q^{m+1}_{\rm sat} - 1 \geq \phi(m+1) - 1 \quad \text{and} \quad \mathcal{Q}(C_{n-m}) \geq q^{n-m}_{\rm sat} \geq \phi(n-m).$$

By using Lemma 6.5(i),(vi) we conclude

$$q^n_{\rm sat} = \mathcal{Q}(C_n) = \mathcal{Q}(C_m) + \mathcal{Q}(C_{n-m}) \geq \phi(m+1) - 1 + \phi(n-m) \geq \phi(n+1) + 1 \geq \phi(n).$$

Step 3: C_n is connected and does not contain any bridging atoms. Since C_n does not contain any bridging atoms, Lemma 6.3 along with the induction hypothesis yields

$$q^n_{\rm sat} = \mathcal{Q}(C_n) \geq q^{n-d-m}_{\rm sat} + m \geq \phi(n-d-m) + m$$

for some $m \geq 4$. By Lemma 6.2 and Lemma 6.5(i),(ii) we then obtain

$$q^n_{\rm sat} \geq \phi(n - 4q^n_{\rm sat} + \eta + 2\#I^{\rm ext}_{\rm ac}) + 4.$$

By Lemma 6.5(ii), $\#I^{\rm ext}_{\rm ac} \geq m \geq 4$, and the fact that η is even we get

$$q^n_{\rm sat} \geq \phi(n - 4q^n_{\rm sat} + \eta + 2\#I^{\rm ext}_{\rm ac}) + 4 \geq \phi(n + 8 - 4q^n_{\rm sat}) + 4. \tag{6.12}$$

Suppose first that $n + 8 - 4q^n_{\rm sat} \leq -1$. Then by Table 1 and (2.13) it is elementary to check that $q^n_{\rm sat} \geq \lceil (n+9)/4 \rceil \geq \phi(n)$. Otherwise, the claim follows from (6.12) and Lemma 6.7 below for $x = q^n_{\rm sat}$, where we note that $n - q^n_{\rm sat}$ is always even. □

In the previous proof we have used the following lemma.

Lemma 6.7. *Let $n \geq 7$. Let $x \in \mathbb{N}$ with $x \leq n/4 + 2$, $n - x$ even, and*

$$x \geq 4 + \phi(n + 8 - 4x). \tag{6.13}$$

Then there holds $x \geq \phi(n)$.

Proof. If $4 + \phi\,(8 + n - 4x) \geq \phi(n)$, the statement follows from (6.13) and if $x \geq \phi(n)$ there is nothing to prove. We now assume by contradiction that

$$\text{(i)} \;\; 4 + \phi\,(8 + n - 4x) < \phi(n) \quad \text{and} \quad \text{(ii)} \;\; x < \phi(n). \tag{6.14}$$

Since $\phi(8+n-4x) - \phi(n)$ is even by (2.13), and $x - \phi(n)$ is even by assumption and (2.13), (6.14) yields

$$\text{(i)} \;\; 6 + \phi\,(8 + n - 4x) \leq \phi(n) \quad \text{and} \quad \text{(ii)} \;\; x \leq \phi(n) - 2. \tag{6.15}$$

Let $n = 1 + 2k^2 + 2k + m$, $m \in \mathbb{N}$, $1 \leq m \leq 4k + 4$. By (6.15)(i) there holds $\phi(n) \geq 6$. Using Table 1, we observe that $n \geq 10$ and thus also $k \geq 1$. We distinguish three cases: (a) $2 \leq m \leq 4k + 4$ and m even. (b) $1 \leq m \leq 2k + 1$, m odd. (c) $2k + 3 \leq m \leq 4k + 3$, m odd.

(a) $2 \leq m \leq 4k + 4$ and m even. By (6.8) there holds $\phi(n) = 3 + 2k$, and (6.15)(ii) thus implies

$$\begin{aligned} 8 + n - 4x &\geq 1 + 2k^2 + 2k + m - 4(\phi(n) - 2) + 8 = 1 + 2k^2 + 2k + m - 4(2k+1) + 8 \\ &= 1 + 2(k-2)^2 + 2(k-2) + m \geq 1 + 2(k-2)^2 + 2(k-2) + 2. \end{aligned}$$

One can also check that the difference of the first and the last expression is even. By Lemma 6.5(ii), (6.15)(i), and $\phi(n) = 3 + 2k$ we then obtain

$$\phi\big(1 + 2(k-2)^2 + 2(k-2) + 2\big) + 6 \leq \phi\,(8 + n - 4x) + 6 \leq \phi(n) = 3 + 2k.$$

For $n \geq 14$ and thus $k \geq 2$, there holds $\phi(1 + 2(k-2)^2 + 2(k-2) + 2) = 3 + 2(k-2)$ by (6.8). This yields the contradiction $5 + 2k \leq 3 + 2k$. A contradiction in the cases $n = 11, 13$, i.e., $k = 1$, can be obtained by noting $1 + 2(k-2)^2 + 2(k-2) + 2 = 3$ and $\phi(3) = 3$, cf. Table 1.

(b) $1 \leq m \leq 2k+1$ *and* m *odd.* By (6.8) there holds $\phi(n) = 2+2k$ and (6.15)(ii) thus yields

$$\begin{aligned} 8+n-4x &\geq 1+2k^2+2k+m-4(\phi(n)-2)+8 = 1+2k^2+2k+m-8k+8 \\ &= 1+2(k-2)^2+2(k-2)+m+4 \geq 1+2(k-2)^2+2(k-2)+1. \end{aligned}$$

The difference of the first and the last expression is even. By Lemma 6.5(ii), (6.15)(i), and $\phi(n) = 2+2k$ we obtain

$$\phi\big(1+2(k-2)^2+2(k-2)+1\big)+6 \leq \phi\left(8+n-4x\right)+6 \leq \phi(n) = 2+2k.$$

For $n \geq 14$ and thus $k \geq 2$, there holds $\phi(1+2(k-2)^2+2(k-2)+1) = 2+2(k-2)$ by (6.8). This yields the contradiction $4+2k \leq 2+2k$. A contradiction in the cases $n = 10, 12$, i.e., $k = 1$, can be obtained by noting $1+2(k-2)^2+2(k-2)+1 = 2$ and $\phi(2) = 2$, cf. Table 1.

(c) $2k+3 \leq m \leq 4k+3$ *and* m *odd.* By (6.8) there holds $\phi(n) = 4+2k$ and (6.15)(ii) thus implies

$$\begin{aligned} 8+n-4x &\geq 1+2k^2+2k+m-4(\phi(n)-2)+8 = 1+2k^2+2k+m-4(2k+2)+8 \\ &= 1+2(k-2)^2+2(k-2)+m-4 \geq 1+2(k-2)^2+2(k-2)+2(k-2)+3. \end{aligned}$$

The difference of the first and the last expression is even. By Lemma 6.5(ii), (6.15)(i), and $\phi(n) = 4+2k$ we obtain

$$\phi\big(1+2(k-2)^2+2(k-2)+2(k-2)+3\big)+6 \leq \phi\left(8+n-4x\right)+6 \leq \phi(n) = 4+2k.$$

For $n \geq 14$ and thus $k \geq 2$, there holds $\phi(1+2(k-2)^2+2(k-2)+2(k-2)+3) = 4+2(k-2)$ by (6.8). This yields the contradiction $6+2k \leq 4+2k$. A contradiction in the cases $n = 10, 12$, i.e., $k = 1$, can be obtained by noting $1+2(k-2)^2+2(k-2)+2(k-2)+3 = 2$ and $\phi(2) = 2$, cf. Table 1. □

6.4. **Crystallization result for q^n_{sat}-optimal configurations.** This subsection is devoted to the proof of Theorem 2.8(a). In Lemma 6.8 we first show that q^n_{sat}-optimal configurations are connected and do not contain bridging atoms after removing a finite number of atoms independently of n. Afterwards, we control the number of non-equilibrated atoms (Lemma 6.9). This then allows us to show Theorem 2.8(a).

Recall that in Proposition 2.5 we have shown that $\phi(n) = q^n_{\mathrm{sat}}$ for all $n \in \mathbb{N}$. In the following, we will use this equality without further notice. As before, it is not restrictive to consider configurations C_n with $\mathcal{Q}(C_n) \geq 0$.

Lemma 6.8 (Connectedness, bridging atoms)**.** *Let C_n be a q^n_{sat}-optimal configuration.*

(a) If $n \geq 11$ and C_n is not connected, we can remove $m \in \{1,2\}$ 0-bonded atoms from C_n to obtain a connected q^{n-m}_{sat}-optimal configuration.

(b) Let $n \geq 26$ and let m_0 be the constant from Lemma 6.5(vii). If C_n contains a bridging atom, there holds $\mathcal{Q}(C_n) \geq \phi(n-26)+2$. We can remove $m \in \{1,\dots,m_0\}$ atoms from C_n to obtain a configuration C_{n-m} which is q^{n-m}_{sat}-optimal and does not contain bridging atoms.

We defer the proof and continue with the next ingredient for the proof of Theorem 2.8(a). We show that the number of non-equilibrated atoms $\mathcal{A}(X_n)$ can be controlled. We remark that the bound on $\mathcal{A}(X_n)$ is not sharp and could be improved at the expense of more elaborated methods. As our focus lies on a qualitative description of the geometry of optimal configurations, we refrain from entering into finer estimates.

Lemma 6.9 (Control on $\#\mathcal{A}(X_n)$)**.** *Let C_n be a q^n_{sat}-optimal configuration without bridging atoms. Then $\#\mathcal{A}(X_n) \leq 50$.*

We again defer the proof and proceed to show Theorem 2.8(a).

Proof of Theorem 2.8(a). Let m_0 be the constant from Lemma 6.5(vii) and define $n_0 = 52m_0+2$. Let C_n be a q^n_{sat}-optimal configuration. If $n < n_0$, the statement is trivial, we therefore suppose that $n \geq n_0$. The goal is to prove that, after removing at most $2m_0+2$ atoms, the remaining configurations is a subset of the square lattice. In view of Lemma 6.8, we can remove $m \leq m_0+2$ atoms from C_n to obtain a connected

configuration C_{n-m} without bridging atoms which is a $q^{n-m}_{\rm sat}$-optimal configuration. Consequently, it suffices to consider a $q^n_{\rm sat}$-configuration C_n, $n \geq 51m_0$, which is connected without bridging atoms and to show that, after removing at most m_0 atoms, it is a subset of the square lattice.

Step 1: Proof for connected configurations without bridging atoms. We introduce

$$\mathcal{X}(X_n) := \{X_m \subset X_n : X_m \text{ connected and } \mathcal{A}(X_m) = \emptyset\}.$$

Note that, if $X_m \in \mathcal{X}(X_n)$, then up to isometry $X_m \subset \mathbb{Z}^2$. Choose $X_n^{\max} \in \mathcal{X}(X_n)$ as a maximal element, that is $\#X_m \leq \#X_n^{\max}$ for all $X_m \in \mathcal{X}(X_n)$. Denote its cardinality by $n_{\max} \leq n$. As C_n is connected and $\#\mathcal{A}(C_n) \leq 50$, it is elementary to see that C_n consists of at most 51 sub-configuration each of which subset of a (different) square lattice. Since $n \geq 51m_0$, this implies $n_{\max} \geq m_0$. Additionally, we set $C_n^{\max} = \{(x_i, q_i) : x_i \in X_n^{\max}\}$. Our goal is now to prove that

$$\#\left(X_n \setminus X_n^{\max}\right) = n - n_{\max} \leq m_0. \tag{6.16}$$

The main ingredient for the proof is the estimate

$$\text{(i)}\quad \mathcal{Q}(C_n^{\max}) \geq \phi(n_{\max}), \qquad \text{(ii)}\quad \mathcal{Q}(C_n \setminus C_n^{\max}) \geq \phi(n - n_{\max} + 50) - 50. \tag{6.17}$$

We defer the proof of (6.17) to Step 2 below and first show (6.16). Assume by contradiction that (6.16) does not hold true, i.e., $n - n_{\max} > m_0$. By (6.17) we obtain

$$\mathcal{Q}(C_n) = \mathcal{Q}(C_n^{\max}) + \mathcal{Q}(C_n \setminus C_n^{\max}) \geq \phi(n_{\max}) + \phi(n - n_{\max} + 50) - 50.$$

Since also $n_{\max} \geq m_0$, we then derive by Lemma 6.5(ii),(vii)

$$\mathcal{Q}(C_n) \geq \phi(n_{\max}) + \phi(n - n_{\max} + 50) - 50 \geq \phi(n + 50) + 2 \geq \phi(n) + 2.$$

This yields $\mathcal{Q}(C_n) \geq q^n_{\rm sat} + 2$ and contradicts $\mathcal{Q}(C_n) = q^n_{\rm sat}$.

Step 2: Proof of (6.17). To conclude the proof, it remains to confirm (6.17). As a preparation, we introduce

$$\mathrm{d}X_n^{\max} := \{x_i \in X_n^{\max} : \mathcal{N}(x_i) \setminus X_n^{\max} \neq \emptyset\},$$

where $\mathcal{N}(x_i)$ (see (2.2)) is defined with respect to X_n. First, we prove that

$$\mathrm{d}X_n^{\max} \subset X_n^+ \cap \mathcal{A}(X_n). \tag{6.18}$$

To see this, let $x_i \in \mathrm{d}X_n^{\max}$ and choose $x_j \in \mathcal{N}(x_i) \setminus X_n^{\max}$. Suppose by contradiction that $x_i \notin \mathcal{A}(X_n)$ or $x_i \in X_n^-$. In both cases, this implies $x_i \notin \mathcal{A}(X_n)$ by Lemma 4.3(a)(i),(iv). Then all bond angles at x_i are integer multiples of $\frac{\pi}{2}$, and thus the configuration $X_n^{\max} \cup \{x_j\}$ is such that $\mathcal{A}(X_n^{\max} \cup \{x_j\}) = \emptyset$. This implies $X_n^{\max} \cup \{x_j\} \in \mathcal{X}(X_n)$ and contradicts the maximality of $\#X_n^{\max}$.

We now show (6.17) and begin with (i). By (6.18) and Lemma 4.3(a)(i) there holds $\#(\mathcal{N}(x_i) \cap X_n^{\max}) = \#\mathcal{N}(x_i) = 4$ for all $x_i \in X_n^{\max}$ with $q_i = -1$, i.e., all negatively charged atoms of $X_n^{\max}$ are 4-bonded. Moreover, since $X_n^{\max} \subset X_n$, $X_n^{\max}$ is repulsion-free and all bonds are unit length by Lemma 4.3(a)(i),(ii). By Lemma 4.3(b) this implies the equality $\mathcal{E}(C_n^{\max}) = -2n_{\max} + 2\mathcal{Q}(C_n^{\max})$. Then Lemma 4.3(a)(iii) yields $\mathcal{Q}(C_n^{\max}) \geq \phi(n_{\max})$, as desired.

We now prove (6.17)(ii). We set $\tilde{X}_n := (X_n \setminus X_n^{\max}) \cup \mathrm{d}X_n^{\max}$ and

$$\tilde{C}_n := \{(x_i, q_i) : x_i \in (X_n \setminus X_n^{\max}) \cup \mathrm{d}X_n^{\max}\}.$$

Since $\mathrm{d}X_n^{\max} \subset X_n^+$ by (6.18), we obtain

$$\mathcal{Q}(\tilde{C}_n) = \mathcal{Q}(C_n \setminus C_n^{\max}) + \#\mathrm{d}X_n^{\max}. \tag{6.19}$$

We now proceed as in the proof of (6.17)(i): let $x_i \in \tilde{X}_n^-$. By (6.18) and Lemma 4.3(a)(i) there holds $\#(\mathcal{N}(x_i) \cap \tilde{X}_n) = \#\mathcal{N}(x_i) = 4$. Since $\tilde{X}_n \subset X_n$, $\tilde{X}_n$ is repulsion-free and all bonds are of unit length by Lemma 4.3(a)(i),(ii). By Lemma 4.3(b) this implies the equality $\mathcal{E}(\tilde{C}_n) = -2\#\tilde{X}_n + 2\mathcal{Q}(\tilde{C}_n)$. Then Lemma 4.3(a)(iii) implies $\mathcal{Q}(\tilde{C}_n) \geq \phi(\#\tilde{X}_n)$.

By (6.18) and Lemma 6.9 we obtain $\#\mathrm{d}X_n^{\max} \le \#\mathcal{A}(X_n) \le 50$. By using (6.19), $\#\tilde{X}_n = n - n_{\max} + \#\mathrm{d}X_n^{\max}$, and applying Lemma 6.5(i) $(50 - \#\mathrm{d}X_n^{\max})$-times, we obtain

$$\begin{aligned}\mathcal{Q}(C_n \setminus C_n^{\max}) &= \mathcal{Q}(\tilde{C}_n) - \#\mathrm{d}X_n^{\max} \ge \phi(\#\tilde{X}_n) - \#\mathrm{d}X_n^{\max}\\ &= \phi(n - n_{\max} + \#\mathrm{d}X_n^{\max}) - \#\mathrm{d}X_n^{\max} \ge \phi(n - n_{\max} + 50) - 50.\end{aligned}$$

This concludes the proof of (6.17)(ii). □

Remark 6.10 (Maximal component)**.** For later purposes, we observe that the configuration $C_n^{\max}$ identified in the proof is a connected subset of the square lattice and that it is saturated, i.e., the atoms with charge -1 are 4-bonded. We also note that $\mathcal{Q}(C_n^{\max}) \le \phi(n_{\max}) + 49$. In fact, otherwise by (6.17)(ii) and Lemma 6.5(ii),(vi) we would get the contradiction $\mathcal{Q}(C_n) \ge \phi(n_{\max}) + 50 + \phi(n - n_{\max} + 50) - 50 \ge \phi(n) + 2$.

We proceed with the proofs of Lemma 6.8 and Lemma 6.9.

Proof of Lemma 6.8. (a) Let $n \ge 11$ and assume by contradiction that C_n is not connected with two connected components of at least three atoms. Denote by C_m and C_{n-m}, $3 \le m, n-m \le n$, two sub-configurations consisting of m and $n-m$ atoms, respectively, with no bonds between them. By Lemma 4.3(a)(vi) we get $\mathcal{Q}(C_m) \ge \phi(m)$ and $\mathcal{Q}(C_{n-m}) \ge \phi(n-m)$. By Lemma 6.5(vi) we obtain

$$\mathcal{Q}(C_n) = \mathcal{Q}(C_m) + \mathcal{Q}(C_{n-m}) \ge \phi(m) + \phi(n-m) \ge 2 + \phi(n) = 2 + q_{\mathrm{sat}}^n.$$

This contradicts $\mathcal{Q}(C_n) = q_{\mathrm{sat}}^n$. Observe that two single atoms may indeed exist, see Fig. 9.

Thus, we can remove $m \in \{1, 2\}$ atoms of charge $+1$ to obtain a connected configuration C_{n-m} with $\mathcal{Q}(C_{n-m}) = \mathcal{Q}(C_n) - m = q_{\mathrm{sat}}^n - m$. By Lemma 6.5(i) this implies $\mathcal{Q}(C_{n-m}) \le q_{\mathrm{sat}}^{n-m}$. On the other hand, by construction, C_{n-m} satisfies

$$\mathcal{E}(C_{n-m}) = \mathcal{E}(C_n) = -2n + 2\mathcal{Q}(C_n) = -2(n-m) + 2\mathcal{Q}(C_{n-m}).$$

Therefore, we get $\mathcal{Q}(C_{n-m}) \ge q_{\mathrm{sat}}^{n-m}$, see Lemma 4.3(a)(iii). Thus, C_{n-m} is q_{sat}^{n-m}-optimal. We also observe that the (at most two) removed atoms are 0-bonded since they all have the same charge $+1$ and C_n has alternating charge distribution.

(b) *Step 1: There exists at most one bridging atom.* Assume by contradiction that there exist two bridging atoms. Denote the two components connected through the first bridging atom by C_{m_1}, C_{n-m_1}, and denote the two components of C_{n-m_1} connected through the second bridging atom by C_{m_2} and $C_{n-m_1-m_2}$, see (6.3). We also observe that, since atoms of charge -1 are 4-bonded (cf. Lemma 4.3(a)(i)), each of the three components contains at least four atoms, i.e., $n \ge n - m_1 - m_2, m_1, m_2 \ge 4$. By Lemma 6.1(a) we get

$$\mathcal{Q}(C_{m_1}) \ge \phi(m_1+1) - 1, \quad \mathcal{Q}(C_{m_2}) \ge \phi(m_2+1) - 1, \quad \mathcal{Q}(C_{n-m_1-m_2}) \ge \phi(n - m_1 - m_2).$$

By using Lemma 6.5(ii) and Lemma 6.5(vi) twice we derive

$$\begin{aligned}\mathcal{Q}(C_n) &\ge \phi(m_1+1) + \phi(m_2+1) + \phi(n-m_1-m_2) - 2 \ge \phi(m_1+m_2+2) + \phi(n-m_1-m_2)\\ &\ge \phi(n+2) + 2 \ge \phi(n) + 2 = 2 + q_{\mathrm{sat}}^n. \quad (6.20)\end{aligned}$$

This contradicts $\mathcal{Q}(C_n) = q_{\mathrm{sat}}^n$.

Step 2: If there exists a bridging atom, then one of the components contains at most m_0 atoms. Assume by contradiction that C_n consists of two components C_m, C_{n-m} connected through a bridging atom with $m, n-m \ge m_0 + 1$. By Lemma 6.1(a) we get $\mathcal{Q}(C_m) \ge \phi(m+1) - 1$ and $\mathcal{Q}(C_{n-m}) \ge \phi(n-m)$. Then Lemma 6.5(i),(vii) yield

$$\mathcal{Q}(C_n) = \mathcal{Q}(C_m) + \mathcal{Q}(C_{n-m}) \ge \phi(m+1) - 1 + \phi(n-m) \ge \phi(n+1) + 51 \ge \phi(n) + 50. \quad (6.21)$$

Thus, $\mathcal{Q}(C_n) > q_{\mathrm{sat}}^n$. This contradicts $\mathcal{Q}(C_n) = q_{\mathrm{sat}}^n$.

Step 3: Conclusion. In view of Step 1 and Step 2, we can remove $m \in \{4, \dots, m_0\}$, $n - m \ge 4$, atoms to obtain a configuration C_{n-m} without bridging atoms. We denote the sub-configuration consisting of the removed atoms by C_m. By Lemma 6.1(a) we get that C_{n-m} is an optimal configuration and $\mathcal{Q}(C_{n-m}) \ge q_{\mathrm{sat}}^{n-m}$. Now suppose by contradiction that $\mathcal{Q}(C_{n-m}) > q_{\mathrm{sat}}^{n-m}$, i.e., $\mathcal{Q}(C_{n-m}) \ge q_{\mathrm{sat}}^{n-m} + 2$.

Recall by Lemma 6.1(a) that $\mathcal{Q}(C_m) \geq \phi(m+1) - 1$. Therefore, since $n \geq m, n-m \geq 4$, by Lemma 6.5(i),(vi) we derive

$$\mathcal{Q}(C_n) = \mathcal{Q}(C_m) + \mathcal{Q}(C_{n-m}) \geq \phi(m+1) - 1 + \phi(n-m) + 2 \geq \phi(n+1) + 3 \geq \phi(n) + 2.$$

This contradicts $\mathcal{Q}(C_n) = q^n_{\rm sat}$ and shows $\mathcal{Q}(C_{n-m}) = q^{n-m}_{\rm sat}$. It remains to prove $\mathcal{Q}(C_n) \geq \phi(n-26)+2$. To see this, we recall by Lemma 6.1(a) that

$$\mathcal{Q}(C_n) \geq \phi(m+1) - 1 + \phi(n-m). \tag{6.22}$$

In view of Lemma 6.5(i),(ii), for $4 \leq m \leq 26$ we derive $\mathcal{Q}(C_n) \geq \phi(m+1)-1+\phi(n-26)-m \bmod 2$. Then the result follows by checking Table 1. If $m \geq 27$, we suppose without restriction that $m+1 \leq n-m$, and we use Lemma 6.5(v) for $n_1 = m+1$, $n_2 = n-m$, $t = n_1 - 27$ to get

$$\phi(m+1) - 1 + \phi(n-m) \geq \phi(m+1-t) + \phi(n-m+t) - 7 = \phi(27) + \phi(n-26) - 7 = \phi(n-26) + 2,$$

where the last step follows from $\phi(27) = 9$, see Table 1. In view of (6.22), this concludes the proof. □

Proof of Lemma 6.9. We prove the statement by induction. For $n \leq 50$ the statement is clearly true. Now let $n \geq 51$. We assume that the statement holds for all $m < n$ and we proceed to prove the statement for n. Let C_n be a $q^n_{\rm sat}$-optimal configuration without bridging atoms. If C_n is not connected, we can apply Lemma 6.8(a) to remove $k \in \{1,2\}$ 0-bonded atoms to obtain a $q^{n-k}_{\rm sat}$-optimal configuration. By the induction hypothesis, this new configuration contains at most 50 non-equilibrated atoms and therefore also $\#\mathcal{A}(X_n) \leq 50$. Therefore, it is not restrictive to assume that C_n is connected. We divide the proof into several steps.

Step 1: $\mathcal{A}(X_n) \cap I_{\rm ac} = \emptyset$ and $\#\mathcal{A}(X_n) \leq 3\eta/2$. We first prove that $\mathcal{A}(X_n) \cap I_{\rm ac} = \emptyset$. By Lemma 6.1(b) there holds $I_{\rm ac} \cap X_n^- = \emptyset$ and $I_{\rm ac} \cap X_n^+$ consists of 1-bonded atoms only. Since 1-bonded atoms do not have bond angles, this implies $I_{\rm ac} \cap \mathcal{A}(X_n) = \emptyset$.

Next, we prove $\#\mathcal{A}(X_n) \leq 3\eta/2$. By Theorem 2.6, Remark 2.2, Lemma 4.2(b), and Lemma 4.3(a)(i),(ii) all squares are regular. Thus, if $x \in \mathcal{A}(X_n)$ is contained in a polygon, this polygon cannot be a square. Moreover, $x \in X_n^+$ by Lemma 4.3(a)(i),(iv). Denote now by f_j the number of j-gons in the bond graph and recall that $f_j = \emptyset$ for j odd or $j \leq 3$. As $\mathcal{A}(X_n) \cap I_{\rm ac} = \emptyset$, each $x \in \mathcal{A}(X_n)$ is contained in at least one j-gon, $j \geq 6$. We also observe that, due to alternating charge distribution, there can be at most $j/2$ atoms of positive charge in each j-gon. This implies by (2.3)

$$\#\mathcal{A}(X_n) \leq \frac{1}{2}\sum_{j\geq 6} j f_j \leq \frac{3}{2}\sum_{j\geq 6}(j-4)f_j = \frac{3}{2}\sum_{j\geq 4}(j-4)f_j = \frac{3}{2}\eta.$$

Step 2: Preliminaries. From now on, we suppose by contradiction that $\#\mathcal{A}(X_n) \geq 51$. This implies $\eta \geq 34$ by Step 1. Note by Lemma 6.3 that $\#I_2 + 2\#I_3 + 3\#I_4 = 2d - m$ and $\#I^{\rm ext}_{\rm ac} \geq m$ for some $m \geq 4$. We will use the following fact several times: the estimate

$$\mathcal{Q}(C_n) \geq \phi(n-d-26-m) + 6 \tag{6.23}$$

along with $\eta \geq 34$ leads to a contradiction: in fact, by Lemma 6.2 and Lemma 6.3 there holds $n - d \in n + 4 - 4\mathcal{Q}(C_n) + \eta + 2\#I^{\rm ext}_{\rm ac} + 2\mathbb{N}_0$ with $\eta \geq 34$ and $\#I^{\rm ext}_{\rm ac} \geq m \geq 4$. Using Lemma 6.5(ii) we obtain

$$\mathcal{Q}(C_n) \geq \phi(n + 8 - 4(\mathcal{Q}(C_n) - 2)) + 6.$$

In view of Lemma 6.7 applied for $x = \mathcal{Q}(C_n) - 2$, we get the contradiction $\phi(n) - 2 = \mathcal{Q}(C_n) - 2 \geq \phi(n)$, see (6.12) for a similar argument.

We denote by C_{n-d-m} the optimal configuration obtained from Lemma 6.3(b) satisfying $\mathcal{A}(X_{n-d-m}) = \mathcal{A}(X_n^{\rm a,bulk})$, $X_{n-d-m} \subset X_n$ up to 0-bonded atoms, and

$$\mathcal{Q}(C_n) = \mathcal{Q}(C_{n-d-m}) + m \geq \phi(n-d-m) + m. \tag{6.24}$$

Note by (2.13), Lemma 6.2, and Lemma 6.3 that $n - d - m \geq n - 4\phi(n) + 4 + \eta + m \geq 26$.

Step 3: C_{n-d-m} satisfies $\mathcal{Q}(C_{n-d-m}) = \phi(n-d-m)$. Assume by contradiction that $\mathcal{Q}(C_{n-d-m}) \geq \phi(n-d-m)+2$. This together with (6.24), $m \geq 4$, and Lemma 6.5(ii) leads to $\mathcal{Q}(C_n) \geq \phi(n-d-m)+6 \geq$

$\phi(n-d-26-m)+6$ which yields a contradiction by (6.23). In view of Lemma 6.8(a), up to removing at most two 0-bonded atoms, we can thus assume that C_{n-d-m} is also connected, and that $X_{n-d-m} \subset X_n$.

Step 4: $\mathcal{A}(X_n) \leq \mathcal{A}(X_n^{\mathrm{a,bulk}}) + 1$, in particular $\mathcal{A}(X_n) \cap \partial X_n^{\mathrm{a}} = \emptyset$. Suppose by contradiction $\mathcal{A}(X_n) \geq \mathcal{A}(X_n^{\mathrm{a,bulk}}) + 2$. By Lemma 6.3(a) we have $m \geq 6$. Thus, by (6.24) and Lemma 6.5(ii) we get $\mathcal{Q}(C_n) \geq \phi(n-d-m)+6 \geq \phi(n-d-26-m)+6$ which yields a contradiction by (6.23). In particular, this also shows $\mathcal{A}(X_n) \cap \partial X_n^{\mathrm{a}} = \emptyset$. Indeed, otherwise we would get $\#(\mathcal{A}(X_n) \cap \partial X_n^{\mathrm{a}}) \geq 2$ by Lemma 4.2 which contradicts $\mathcal{A}(X_n) \leq \mathcal{A}(X_n^{\mathrm{a,bulk}}) + 1$.

Step 5: C_{n-d-m} contains a bridging atom. Suppose by contradiction that C_{n-d-m} does not contain a bridging atom. By Step 3 and Step 4 we get that

$$51 \leq \#\mathcal{A}(X_n) \leq \#\mathcal{A}(X_n^{\mathrm{a,bulk}}) + 1 = \#\mathcal{A}(X_{n-d-m}) + 1 \tag{6.25}$$

and $\mathcal{Q}(C_{n-d-m}) = \phi(n-d-m)$. (The equality in (6.25) follows from Lemma 6.3(b).) By the induction hypothesis applied on C_{n-d-m}, we get $\mathcal{A}(X_{n-d-m}) \leq 50$. This implies equality in (6.25), i.e., $50 = \#\mathcal{A}(X_n) - 1 = \mathcal{A}(X_{n-d-m})$. Note that this together with Step 1 yields $\eta(C_{n-d-m}) \geq 34$. By Step 4 (applied for X_{n-d-m} in place of X_n; note that C_{n-d-m} is connected, q_{sat}^{n-d-m}-optimal, without bridging atoms, and $\eta(C_{n-d-m}) \geq 34$) we also get $\mathcal{A}(X_{n-d-m}) \cap \partial X_{n-d-m}^{\mathrm{a}} = \emptyset$.

Consider the unique $x \in \mathcal{A}(X_n) \setminus \mathcal{A}(X_n^{\mathrm{a,bulk}})$. Since X_n does not contain bridging atoms and all elements in $\mathcal{A}(X_n)$ are at least 2-bonded, x is contained in an elementary polygon P. By Lemma 4.2 we find some $y \in \mathcal{A}(X_n) \cap (P \setminus \{x\})$. We now show that y is a bridging atom in X_{n-d-m}. Note first that $y \in \mathcal{A}(X_{n-d-m})$ since otherwise there would hold strict inequality in (6.25). Observe by Lemma 4.3(a)(iv),(v) that y is 2-bonded. Then, it is also clear that $P \cap X_{n-d-m}$ is contained in the boundary of the exterior face. Therefore, y has to be an acyclic atom since otherwise we obtain the contradiction $\mathcal{A}(X_{n-d-m}) \cap \partial X_{n-d-m}^{\mathrm{a}} \neq \emptyset$. This shows that the configuration C_{n-d-m} contains the bridging atom y. This contradicts our assumption that C_{n-d-m} does not contain bridging atoms. Summarizing, C_{n-d-m} needs to contain a bridging atom.

Step 6: $\#\mathcal{A}(X_n) \leq 50$. Recall that we have supposed by contradiction that $\#\mathcal{A}(X_n) \geq 51$ which implies $\eta \geq 34$ by Step 1. By Lemma 6.8(b) we obtain $\mathcal{Q}(C_{n-d-m}) \geq \phi(n-d-m-26)+2$. This along with (6.24) and $m \geq 4$ gives

$$\mathcal{Q}(C_n) \geq \phi(n-d-26-m) + m + 2 \geq \phi(n-d-26-m) + 6,$$

which leads to a contradiction by (6.23). □

Remark 6.11 (Theorem 2.8(a) without bridging atoms)**.** By increasing n_0 independently of n, the configuration in Theorem 2.8(a) can constructed to be a connected, saturated subset of the square lattice without bridging atoms: the configuration $C_n^{\max}$ in Remark 6.10 may contain at most 49 bridging atoms. In fact, otherwise one could apply Lemma 6.1(a) and Lemma 6.5(vi) 50 times to obtain an estimate of the form (see (6.20) for a similar argument)

$$\mathcal{Q}(C_n^{\max}) \geq \phi(n_{\max} + 50) + 50 \geq \phi(n_{\max}) + 50, \tag{6.26}$$

which contradicts $\mathcal{Q}(C_n^{\max}) \leq \phi(n_{\max}) + 49$. In a similar fashion, repeating the arguments in (6.21), one of the components connected through a bridging atom has at most m_0 atoms as otherwise (6.26) holds. Thus, it suffices to remove at most $49m_0$ atoms to get the desired configuration without bridging atoms.

6.5. **Wulff-shape emergence for q_{sat}^n-optimal configurations.** This subsection is devoted to the proof of Theorem 2.8(b). Our strategy is to apply an anisotropic quantitative isoperimetric inequality on suitable interpolations of the configurations. (A similar idea can be found in [7].) We first state two lemmas which relate the ∞-perimeter of the interpolation to the net charge and then prove the main result. Recall that configurations are called saturated if the atoms of the minority phase are 4-bonded. We also recall (2.3).

Lemma 6.12 (Control on η)**.** *Let $N_1 \in \mathbb{N}$. Let C_n be a connected and saturated sub-configuration of the square lattice without bridging atoms satisfying*

$$0 \leq \mathcal{Q}(C_n) \leq \phi(n) + N_1. \tag{6.27}$$

Then there exists $N_2 = N_2(N_1) > 0$ such that we can add $k \le N_2$ atoms to C_n to obtain a connected, saturated sub-configuration C_{n+k} of the square lattice without bridging atoms satisfying $\mathcal{Q}(C_{n+k}) \ge 0$ and $\eta(C_{n+k}) = 0$.

We defer the proof to the end of the subsection. A key ingredient for the proof of Theorem 2.8(b) is that, for (special) saturated configurations, the net charge coincides with the ∞-perimeter of a suitable interpolation of the configuration. We define $D(x) := \{|x - \cdot|_1 \le 1\}$ for $x \in \mathbb{Z}^2$. For a saturated configuration C_n with $\mathcal{Q}(C_n) \ge 0$ we introduce the interpolation

$$A(C_n) := \bigcup_{q_i=-1} D(x_i) \tag{6.28}$$

and define the ∞-perimeter by

$$\mathrm{Per}_\infty(A(C_n)) := \int_{\partial A(C_n)} |\nu_{A(C_n)}|_\infty \,\mathrm{d}\mathcal{H}^1 = \tfrac{1}{\sqrt{2}}\mathcal{H}^1(\partial A(C_n)). \tag{6.29}$$

Here, $\nu_{\partial A(C_n)}$ is the outer unit normal to the set $A(C_n)$. The second identity in (6.29) is elementary since by definition there holds $|(\nu_{\partial A(C_n)})_1(x)| = |(\nu_{\partial A(C_n)})_2(x)| = 1/\sqrt{2}$ for $\mathcal{H}^1$-almost every point $x \in \partial A(C_n)$.

Lemma 6.13. *Let C_n be a saturated, connected sub-configuration of the square lattice which does not contain bridging atoms and satisfies $\eta = 0$ as well as $\mathcal{Q}(C_n) \ge 0$. Then $\mathrm{Per}_\infty(A(C_n)) = 2\mathcal{Q}(C_n) - 2$.*

We again defer the proof and proceed to show Theorem 2.8(b).

Proof of Theorem 2.8(b). Our strategy is to apply an anisotropic quantitative isoperimetric inequality on $A(C_n)$, defined in (6.28). To this end, we will modify a given q^n_{sat}-optimal configuration such that Lemma 6.13 is applicable. We split the proof into three steps. In the following, c denotes a universal constant which may vary from line to line, but is independent of n.

Step 1: Some elementary facts. For $n \in \mathbb{N}$ we set

$$\underline{n} = \max\{N \le n :\ N = 1 + 2k^2 + 2k,\ k \in \mathbb{N}\}.$$

A careful inspection of (6.8) yields for all $n \in \mathbb{N}$

$$\text{(i)}\ \ \phi(\underline{n}) \le \phi(n) \le \phi(\underline{n}) + 3, \qquad \text{(ii)}\ \ \underline{n} - \phi(\underline{n}) \le n - \phi(n) \le \underline{n} - \phi(\underline{n}) + c\sqrt{n}. \tag{6.30}$$

Let C'_n be a saturated configuration with $\mathcal{Q}(C'_n) \ge 0$. We find $\mathcal{L}^2(A(C'_n)) = 2\#\{q_i = -1\}$ since $\mathcal{L}^2(D(x)) = 2$ for all $x \in \mathbb{Z}^2$. Thus, $\mathcal{L}^2(A(C'_n)) = n - \mathcal{Q}(C'_n)$. We let $W_r := \{|\cdot|_1 \le r\}$ and note that

$$\mathcal{L}^2\big(W_{r(C'_n)}\big) = 2r(C'_n)^2 = \mathcal{L}^2(A(C'_n)), \qquad \text{where}\ \ r(C'_n) := \sqrt{\tfrac{1}{2}(n - \mathcal{Q}(C'_n))}. \tag{6.31}$$

Step 2: Modification of q^n_{sat}-optimal configurations. Let C_n be a q^n_{sat}-optimal configuration. By Remark 6.11, after removing at most n_0 atoms, we get a saturated, connected sub-configuration of the square lattice C_{n-m}, $0 \le m \le n_0$, whose bond graph does not contain any bridging atoms. By Lemma 6.5(i) there holds

$$0 \le \mathcal{Q}(C_{n-m}) \le \phi(n) + m \le \phi(n-m) + 2m \le \phi(n-m) + 2n_0.$$

By Lemma 6.12 we can add at most $N_2(2n_0)$ atoms to obtain a saturated, connected sub-configuration of the square lattice without bridging atoms satisfying $\eta = 0$. For simplicity, we denote the configuration again by C_n and observe that

$$|\mathcal{Q}(C_n) - \phi(n)| \le c. \tag{6.32}$$

In Step 3 below we will apply Lemma 6.13 on C_n. The newly constructed configuration and the original configuration differ in cardinality and net charge by a finite constant independent of n, i.e., it suffices to prove the statement for this new configuration.

Step 3: Application of the quantitative isoperimetric inequality. Recall that the diamond $D_{\underline{n}}$ with alternating charge distribution is a $q^{\underline{n}}_{\mathrm{sat}}$-optimal configuration, see (2.9) and Subsection 3.3. By (6.30)(ii), (6.31), and (6.32) this implies $r(D_{\underline{n}})^2 - c \le r(C_n)^2 \le r(D_{\underline{n}})^2 + c\sqrt{n}$. Therefore, we get

$$\text{(i)}\ \ \mathrm{Per}_\infty(A(D_{\underline{n}})) \le \mathrm{Per}_\infty(W_{r_n}) + c, \qquad \text{(ii)}\ \ \mathcal{L}^2(W_{r_n} \triangle A(D_{\underline{n}})) \le c\sqrt{n}, \tag{6.33}$$

where for brevity we have set $r_n = r(C_n)$. Using the definition $r_n = \sqrt{\frac{1}{2}(n - \mathcal{Q}(C_n))}$, (2.13), and (6.32) one can also check that for n sufficiently large there holds

$$r_n \in (\tfrac{1}{2}\sqrt{n/2}, \sqrt{n/2}). \tag{6.34}$$

By the quantitative anisotropic isoperimetric inequality [13, Theorem 1.1] (applied for the convex set $K = W_1$) there exists a translation $\tau \in \mathbb{R}^2$ such that

$$(\mathcal{L}^2(W_{r_n}))^{-2}\mathcal{L}^2(W_{r_n} \triangle (A(C_n) + \tau))^2 \le c\,\mathrm{Per}_\infty(W_{r_n})^{-1}\big(\mathrm{Per}_\infty(A(C_n)) - \mathrm{Per}_\infty(W_{r_n})\big).$$

As by (6.29), (6.31), and (6.34) there holds $\mathcal{L}^2(W_{r_n}) = 2r_n^2 \le n$ and $\mathrm{Per}_\infty(W_{r_n}) = 4r_n \ge 2\sqrt{n/2}$, we get

$$\mathcal{L}^2(W_{r_n} \triangle (A(C_n) + \tau))^2 \le cn^{3/2}\,\big(\mathrm{Per}_\infty(A(C_n)) - \mathrm{Per}_\infty(W_{r_n})\big). \tag{6.35}$$

To estimate the right hand side, we apply Lemma 6.13 (on both C_n and $D_{\underline{n}}$), (6.30)(i), (6.32), (6.33)(i), and $\phi(\underline{n}) = \mathcal{Q}(D_{\underline{n}})$ to get

$$\begin{aligned}\mathrm{Per}_\infty(A(C_n)) - \mathrm{Per}_\infty(W_{r_n}) &\le \mathrm{Per}_\infty(A(C_n)) - \mathrm{Per}_\infty(A(D_{\underline{n}})) + c = 2\mathcal{Q}(C_n) - 2\mathcal{Q}(D_{\underline{n}}) + c \\ &\le 2(\phi(n) - \phi(\underline{n})) + c \le c.\end{aligned} \tag{6.36}$$

After translation we may suppose that $X_n + \tau$ and $D_{\underline{n}}$ are both contained in $\mathbb{Z}^2$. By the fact that $\mathcal{L}^2(D(x)) = 2$ for all $x \in \mathbb{Z}^2$, (6.28), (6.33)(ii), (6.35), and (6.36) we get

$$2\,\#\big(D^-_{\underline{n}} \triangle (X^-_n + \tau)\big) = \mathcal{L}^2(A(D_{\underline{n}}) \triangle (A(C_n) + \tau)) \le \mathcal{L}^2(W_{r_n} \triangle (A(C_n) + \tau)) + \mathcal{L}^2(W_{r_n} \triangle A(D_{\underline{n}})) \le Cn^{3/4}.$$

It remains to note that $\#(D_{\underline{n}} \triangle (X_n + \tau)) \le 5\,\#(D^-_{\underline{n}} \triangle (X^-_n + \tau))$ since C_n is saturated. □

It remains to prove Lemma 6.12 and Lemma 6.13.

Proof of Lemma 6.12. We first construct the configuration C_{n+k}. By X^{int}_n we denote the union of the points $\mathbb{Z}^2 \setminus X_n$ which are contained in the interior of a simple cycle of the bond graph of X_n. Let $C^{\mathrm{int}}_n = (X^{\mathrm{int}}_n, Q^{\mathrm{int}})$, where Q^{int} is chosen such that $C_n \cup C^{\mathrm{int}}_n$ has alternating charge distribution. This is possible since $X_n \cup X^{\mathrm{int}}_n \subset \mathbb{Z}^2$. Define $k := \#X^{\mathrm{int}}_n$ and $C_{n+k} := C_n \cup C^{\mathrm{int}}_n$. Note that C_{n+k} is still connected, saturated and does not contain bridging atoms. Moreover, C_{n+k} has alternating charge distribution, is subset of the square lattice, and $\eta(C_n \cup C^{\mathrm{int}}_n) = 0$. Therefore, the configuration satisfies Lemma 4.3(a)(i),(ii). Hence, Lemma 4.3(b),(a)(iii) implies

$$\mathcal{Q}(C_{n+k}) \ge \phi(n+k). \tag{6.37}$$

It remains to control k. Choose $N_2 \in \mathbb{N}$ depending only on N_1 such that

$$\phi(N_2 + 1) \ge N_1 + 3. \tag{6.38}$$

We now assume by contradiction that $k \ge N_2 + 1$. We claim that

$$\mathcal{Q}(C^{\mathrm{int}}_n) \le -\phi(k). \tag{6.39}$$

We postpone the proof of this estimate to the end and proceed to establish a contradiction. Using (6.27) and (6.37)-(6.39) we obtain

$$\phi(n+k) \le \mathcal{Q}(C_{n+k}) = \mathcal{Q}(C_n) + \mathcal{Q}(C^{\mathrm{int}}_n) \le \phi(n) + N_1 - \phi(k). \tag{6.40}$$

Now by $k \ge N_2 + 1$, Lemma 6.5(i),(ii), and (6.38) there holds $\phi(k) \ge \phi(N_2 + 1) - 1 \ge N_1 + 2$. This together with (6.40) leads to $\phi(n+k) \le \phi(n) - 2$ which contradicts Lemma 6.5(i),(ii).

It remains to prove (6.39). By construction there holds $X^{\mathrm{int}}_n \subset \mathbb{Z}^2$. In particular, the configuration is repulsion-free and all bonds have unit length. In view of Lemma 4.3(b),(a)(iii) (note that it is applicable even though the configuration has negative net charge: consider $(X^{\mathrm{int}}_n, -Q^{\mathrm{int}})$), it remains to show that each $x \in (X^{\mathrm{int}}_n)^+$ has four neighbors in X^{int}_n. If there existed some $x \in (X^{\mathrm{int}}_n)^+$ which is at most 3-bonded,

then there would exist $y \in X_n^-$ such that $|x-y|=1$. Since every point on the square lattices has at most four neighboring points on the square lattice, this would imply that y is not 4-bonded and thus X_n would not have been a saturated configuration: a contradiction. □

Proof of Lemma 6.13. We prove the claim by induction over $k = \#X_n^-$. Let $k=1$. As C_n is connected, this implies $n=5$ and therefore $\mathcal{Q}(C_n)=3$ as well as $\mathrm{Per}_\infty(A(C_n))=4$. Thus, the claim is true for $k=1$. Now assume that we have proved the statement for all $l<k$. We proceed to prove the claim for k. Consider the leftmost of the uppermost negatively charged atoms and denote it by x_0. There are three cases to consider (see Fig. 12):

(a) $D(x_0)$ shares exactly one side with another square $D(x_1)$, $x_1 \in X_n^-$.
(b) $D(x_0)$ shares exactly two adjacent sides with two other squares $D(x_1), D(x_2)$, $x_1, x_2 \in X_n^-$. The atom which is contained in both of these sides is contained in four squares.
(c) $D(x_0)$ shares exactly two adjacent sides with two other squares $D(x_1), D(x_2)$, $x_1, x_2 \in X_n^-$. The atom which is contained in both of these sides is contained in only three squares.

This is a consequence of the choice of x_0, the absence of bridging atoms, the connectedness of C_n, and $\eta=0$. In fact, by the choice of the point x_0, the top corner cannot be contained in another square. Next, at least one side of $D(x_0)$ has to be shared with another square since otherwise the configuration would not be connected or there would be a 2-bonded atom. The latter in turn would be a bridging atom or would lead to $\eta \geq 2$. Finally, if $D(x_0)$ shares exactly two sides with other squares, the bottom corner is either contained in three or four squares.

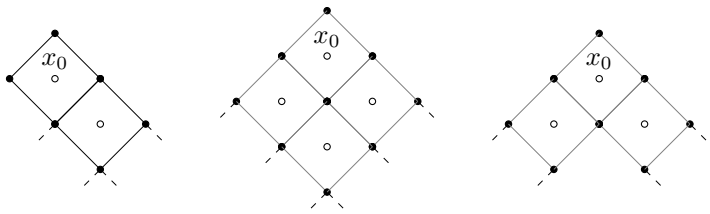

FIGURE 12. The three cases (a)-(c). Case (a) holds up to reflection.

Proof of (a): We remove the two corners of positive charge not contained in any other square as well as x_0 to obtain a configuration C_{n-3} such that $\#X_{n-3}^- = k-1$. Note that

$$\mathcal{Q}(C_{n-3}) = \mathcal{Q}(C_n) - 1. \tag{6.41}$$

Since we have removed three sides of the square $D(x_0)$ but count a side of the square $D(x_1)$ to the perimeter, we obtain

$$\mathrm{Per}_\infty(A(C_{n-3})) = \mathrm{Per}_\infty(A(C_n)) - 2. \tag{6.42}$$

It is elementary to check that the new configuration is still saturated, connected, satisfies $\eta(C_{n-3})=0$, and does not contain any bridging atom. Therefore, we can apply the induction hypothesis together with (6.41) and (6.42) to obtain

$$\mathrm{Per}_\infty(A(C_n)) = \mathrm{Per}_\infty(A(C_{n-3})) + 2 = 2\mathcal{Q}(C_{n-3}) = 2\mathcal{Q}(C_n) - 2.$$

Proof of (b): We remove the top corner of positive charge as well as x_0 to obtain a configuration C_{n-2} such that $\#X_{n-2}^- = k-1$. Again, the new configuration is still saturated, connected, satisfies $\eta(C_{n-2})=0$, and does not contain any bridging atom. We get $\mathcal{Q}(C_{n-2}) = \mathcal{Q}(C_n)$ and, since we have removed two sides of the square $D(x_0)$ but count one side of each square $D(x_1)$, $D(x_2)$ to the perimeter, we obtain $\mathrm{Per}_\infty(A(C_{n-2})) = \mathrm{Per}_\infty(A(C_n))$. This along with the induction hypothesis yields

$$\mathrm{Per}_\infty(A(C_n)) = \mathrm{Per}_\infty(A(C_{n-2})) = 2\mathcal{Q}(C_{n-2}) - 2 = 2\mathcal{Q}(C_n) - 2.$$

Proof of (c): We remove the top corner of positive charge as well as x_0 to obtain two sub-configurations C_{m_1},C_{m_2} which share only the bottom atom of $D(x_0)$. This implies $m_1+m_2=n-1$ and

$$\mathcal{Q}(C_{m_1})+\mathcal{Q}(C_{m_2})=\mathcal{Q}(C_n)+1. \tag{6.43}$$

We again observe that the new configurations are saturated, connected, satisfy $\eta(C_{m_1})=\eta(C_{m_2})=0$, and do not contain any bridging atom. (Note that the configuration obtained by removing the top corner and x_0 would contain one bridging atom.) We have removed two sides of the square $D(x_0)$, but count one side of $D(x_1)$ to the perimeter of C_{m_1} and count one side of $D(x_2)$ to the perimeter of C_{m_2}. This implies

$$\mathrm{Per}_\infty(A(C_{m_1}))+\mathrm{Per}_\infty(A(C_{m_2}))=\mathrm{Per}_\infty(A(C_n)). \tag{6.44}$$

Note that $\#X^-_{m_1},\#X^-_{m_2}<k$. Thus, we can use the induction hypothesis along with (6.43)-(6.44) to obtain

$$\mathrm{Per}_\infty(A(C_n))=\mathrm{Per}_\infty(A(C_{m_1}))+\mathrm{Per}_\infty(A(C_{m_2}))=2\mathcal{Q}(C_{m_1})-2+2\mathcal{Q}(C_{m_2})-2=2\mathcal{Q}(C_n)-2.$$

This concludes the proof. □

Appendix A. Proof of the boundary energy and net charge estimates

This section is devoted to the proofs of Lemma 5.3 and Lemma 6.3.

Proof of Lemma 5.3. For convenience, we decompose the proof into three steps.

Step 1: Preliminary estimate. Assume that C_n is a connected ground state with no acyclic bonds. Suppose that $\{x_1,\dots,x_d\}$ are ordered such that $x_i\in\mathcal{N}(x_{i+1})$, $i=1,\dots,d$. Here and in the following, we use the identification $x_{d+1}=x_1$ and $x_0=x_d$. For a 3-bonded atom x_i, denote by $x_i^b\in X_n\setminus\{x_{i-1},x_{i+1}\}$ the atom that is connected to x_i with the third bond. In a similar fashion, for a 4-bonded atom x_i, denote by $x_i^{b,1},x_i^{b,2}\in X_n\setminus\{x_{i-1},x_{i+1}\}$ the two atoms which are bonded to x_i. Recall (5.1)-(5.3) and Remark 5.2. We first observe that the boundary energy can be estimated by

$$\begin{aligned}\mathcal{R}^{\mathrm{bnd}}(C_n)\geq\sum_{i=1}^d\Big(&\frac{1}{2}\big(V_{\mathrm{a}}(|x_i-x_{i+1}|)+V_{\mathrm{a}}(|x_i-x_{i-1}|)\big)+\frac{1}{4}V_{\mathrm{r}}(|x_{i+1}-x_{i-1}|)\Big)\\&+\sum_{x_i\in I_3}\Big(V_{\mathrm{a}}(|x_i-x_i^b|)+\frac{1}{4}\big(V_{\mathrm{r}}(|x_{i-1}-x_i^b|)+V_{\mathrm{r}}(|x_{i+1}-x_i^b|)\big)\Big)\\&+\sum_{x_i\in I_4}\Big(V_{\mathrm{a}}(|x_i-x_i^{b,1}|)+V_{\mathrm{a}}(|x_i-x_i^{b,2}|)\\&\qquad+\frac{1}{4}\big(V_{\mathrm{r}}(|x_{i-1}-x_i^{b,1}|)+V_{\mathrm{r}}(|x_i^{b,1}-x_i^{b,2}|)+V_{\mathrm{r}}(|x_{i+1}-x_i^{b,2}|)\big)\Big).\end{aligned} \tag{A.1}$$

For a 3-bonded atom x_i, denote by $\theta_i^1,\theta_i^2\in[0,2\pi]$ the angle between x_{i-1},x_i,x_i^b and the angle between x_i^b,x_i,x_{i+1} respectively. For a 4-bonded atom x_i, denote by $\theta_i^1,\theta_i^2,\theta_i^3\in[0,2\pi]$ the angle between $x_{i-1},x_i,x_i^{b,1}$, the angle between $x_i^{b,1},x_i,x_i^{b,2}$ and the angle between $x_i^{b,2},x_i,x_{i+1}$, respectively. Finally, we define $\delta:=(\#I_2+2\#I_3+3\#I_4)/d$ and note that $\delta\in[1,3]$ since $\#I_2+\#I_3+\#I_4=d$. We will prove that

$$\begin{aligned}\mathcal{R}^{\mathrm{bnd}}(C_n)&\geq-\delta d+\frac{1}{4}\Big(\sum_{x_i\in I_2}V_{\mathrm{r}}\Big(2\sin\Big(\frac{\theta_i}{2}\Big)\Big)+\sum_{x_i\in I_3}\sum_{j=1}^2V_{\mathrm{r}}\Big(2\sin\Big(\frac{\theta_i^j}{2}\Big)\Big)+\sum_{x_i\in I_4}\sum_{j=1}^3V_{\mathrm{r}}\Big(2\sin\Big(\frac{\theta_i^j}{2}\Big)\Big)\Big)\\&\geq-\delta d+\frac{1}{4}\delta d\,V_{\mathrm{r}}\Big(2\sin\Big(\frac{\pi(d-2)}{2\delta d}\Big)\Big),\end{aligned} \tag{A.2}$$

where the first inequality is strict if not all lengths of boundary bonds are equal to 1. We defer the proof of (A.2) to Step 3. At this stage, let us only point out that the specific definition of the boundary energy including also bulk bonds, see Remark 5.2 and Fig. 10, ensures that also θ_i^2, $x_i\in I_4$, gives a contribution.

Step 2: Proof of the statement. We now show that (A.2) implies the statement of the lemma. First, we introduce

$$\alpha(\delta) := \frac{\pi(d-2)}{2\delta d},$$

and observe that estimate (A.2) can be written as

$$\mathcal{R}^{\mathrm{bnd}}(C_n) \geq -\delta d + \frac{1}{4}\delta d\, V_{\mathrm{r}}\Big(2\sin\Big(\frac{\pi(d-2)}{2\delta d}\Big)\Big) = \delta d\Big(\frac{1}{4}V_{\mathrm{r}}\big(2\sin(\alpha(\delta))\big) - 1\Big). \tag{A.3}$$

We obtain (5.4) by minimizing the right hand side of (A.3) with respect to δ. To see this, set $\delta_0 = 2 - \frac{4}{d}$. For $1 \leq \delta \leq \delta_0$, we have $\alpha(\delta_0) = \frac{\pi}{4} \leq \alpha(\delta) \leq \frac{\pi}{2}$. By [vii] we get $V_{\mathrm{r}}(2\sin(\alpha(\delta))) = 0$ for all $1 \leq \delta \leq \delta_0$. Therefore, we find

$$\delta d\Big(\frac{1}{4}V_{\mathrm{r}}(2\sin(\alpha(\delta))) - 1\Big) = -\delta d \geq -\delta_0 d = -(2d-4) \tag{A.4}$$

and we obtain (5.4) for $1 \leq \delta \leq \delta_0$. Now for $\delta_0 < \delta \leq 3$, we have $\alpha(\delta) < \alpha(\delta_0)$. By (v) we get

$$V_{\mathrm{r}}\big(2\sin(\alpha(\delta))\big) \geq V_{\mathrm{r}}\big(2\sin(\alpha(\delta_0))\big) + 2V'_{\mathrm{r},-}\big(2\sin(\alpha(\delta_0))\big)\big(\sin(\alpha(\delta)) - \sin(\alpha(\delta_0))\big).$$

Then by the fact that $\sin(\theta)$ is concave for $\theta \in [0,\pi]$, $V_{\mathrm{r}}(\sqrt{2}) = 0$ by [vii], $V'_{\mathrm{r},-}(\sqrt{2}) < -16/(\sqrt{2}\pi) < 0$ by [viii], $\alpha(\delta_0) = \frac{\pi}{4}$, $\sin(\alpha(\delta_0)) = \cos(\alpha(\delta_0)) = \frac{1}{2}\sqrt{2}$, and $\alpha(\delta) - \alpha(\delta_0) < 0$ we derive

$$\begin{aligned} V_{\mathrm{r}}(2\sin(\alpha(\delta))) &\geq V_{\mathrm{r}}(\sqrt{2}) + 2V'_{\mathrm{r},-}(\sqrt{2})\cos(\alpha(\delta_0))\big(\alpha(\delta) - \alpha(\delta_0)\big) \\ &= V_{\mathrm{r}}(\sqrt{2}) + \sqrt{2}\,V'_{\mathrm{r},-}(\sqrt{2})\Big(\frac{\pi(d-2)}{2\delta d} - \frac{\pi}{4}\Big) > -\frac{16}{\pi}\Big(\frac{\pi(d-2)}{2\delta d} - \frac{\pi}{4}\Big) \\ &= \frac{4}{\delta d}(\delta d - 2d + 4). \end{aligned} \tag{A.5}$$

From the previous calculation and (A.3), estimate (5.4) follows also for $\delta_0 < \delta \leq 3$.

We now show that we have strict inequality in (5.4) if one of the conditions (5.5)-(5.7) is violated. First, if a boundary bond is not of unit length, we have strict inequality in (A.2) and thus also in (A.3). If (5.6) is violated, we find $\delta \neq \delta_0$ after a short computation. Then we get strict inequalities from (A.4) or (A.5), respectively. Finally, let use assume that (5.7) is violated. We can suppose that $\delta = \delta_0$ and (5.5)-(5.6) hold as otherwise the inequality in (5.4) is strict. If equality holds in (5.4), then equality also holds in (A.2). As $V_{\mathrm{r}}(2\sin(\alpha(\delta_0))) = 0$, this implies

$$\sum_{x_i \in I_2} V_{\mathrm{r}}\Big(2\sin\Big(\frac{\theta_i}{2}\Big)\Big) + \sum_{x_i \in I_3}\sum_{j=1}^{2}\Big(V_{\mathrm{r}}\Big(2\sin\Big(\frac{\theta_i^j}{2}\Big)\Big) + \sum_{x_i \in I_4}\sum_{j=1}^{3} V_{\mathrm{r}}\Big(2\sin\Big(\frac{\theta_i^j}{2}\Big)\Big)\Big) = 0.$$

In view of [vii], this gives

$$\theta_i \in [\tfrac{\pi}{2}, \tfrac{3\pi}{2}] \ \text{ for } x_i \in I_2, \qquad \theta_i^1, \theta_i^2 \in [\tfrac{\pi}{2}, \tfrac{3\pi}{2}] \ \text{ for } x_i \in I_3, \qquad \theta_i^1, \theta_i^2, \theta_i^3 \in [\tfrac{\pi}{2}, \tfrac{3\pi}{2}] \ \text{ for } x_i \in I_4. \tag{A.6}$$

Under the assumption that (5.7) is violated, in view of (A.6), $\theta_i = \theta_i^1 + \theta_i^2$ for $x_i \in I_3$ and $\theta_i = \theta_i^1 + \theta_i^2 + \theta_i^3$ for $x_i \in I_4$ we obtain

$$\begin{aligned} \pi(d-2) = \sum_{i=1}^{d}\theta_i &= \sum_{x_i \in I_2}\theta_i + \sum_{x_i \in I_3}(\theta_i^1 + \theta_i^2) + \sum_{x_i \in I_4}(\theta_i^1 + \theta_i^2 + \theta_i^3) \\ &> \frac{\pi}{2}\#I_2 + \pi\#I_3 + \frac{3\pi}{2}\#I_4 = \pi(d-2), \end{aligned}$$

where the first equality follows from the fact that the maximal polygon has d vertices, and the last equality holds by (5.6). This is a contradiction and shows that strict inequality in (5.4) holds if (5.7) is violated.

Step 3: Proof of (A.2). To complete the proof, it remains to show (A.2). We follow the lines of the proof of [16, Lemma 5.1]. In the case of a 2-bonded x_i, define $r_i^1 = |x_i - x_{i-1}|$ and $r_i^2 = |x_i - x_{i+1}|$. In the case

of a 3-bonded x_i, define additionally $r_i^3 = |x_i^b - x_i|$. In the case of a 4-bonded x_i, define $r_i^3 = |x_i^{b,1} - x_i|$ and $r_i^4 = |x_i^{b,2} - x_i|$. By the cosine rule we obtain

$$\begin{aligned}
&|x_{i+1} - x_{i-1}| = \ell(\theta_i, r_i^1, r_i^2), \text{ for } x_i \in \partial X_n,\\
&|x_i^b - x_{i-1}| = \ell(\theta_i^1, r_i^1, r_i^3),\ |x_i^b - x_{i+1}| = \ell(\theta_i^2, r_i^2, r_i^3) \text{ for } x_i \in I_3,\\
&|x_i^{b,1} - x_{i-1}| = \ell(\theta_i^1, r_i^1, r_i^3),\ |x_i^{b,1} - x_i^{b,2}| = \ell(\theta_i^2, r_i^3, r_i^4),\ |x_i^{b,2} - x_{i+1}| = \ell(\theta_i^3, r_i^2, r_i^4) \text{ for } x_i \in I_4,
\end{aligned} \tag{A.7}$$

where we have used the shorthand

$$\ell(\theta, r_1, r_2) = \sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos(\theta)}. \tag{A.8}$$

We want to prove that for every boundary atom x_i its contribution to the energy can be controlled by the energy contribution in a modified configuration which has the same angles but unit bond lengths instead of r_i^1, r_i^2. Recall that by [viii] we have for all $r \in (1, r_0]$

$$\frac{2}{r-1}(V_{\mathrm{a}}(1) - V_{\mathrm{a}}(r)) < V'_{\mathrm{r},+}(1). \tag{A.9}$$

As we consider finite energy configurations, by [i],[iv], it is not restrictive to assume that $\ell(\theta, r_1, r_2) \geq 1$. Note that $V'_{\mathrm{r},+}(r) \leq 0$ for $r \geq 1$ and $V'_{\mathrm{r},+}$ is monotone increasing due to the convexity assumption in (v) on V_{r}. Moreover, we have $\partial_{r_1}\ell(\theta, r_1, r_2) \leq 1$ by an elementary computation. We therefore obtain

$$\frac{2}{r-1}(V_{\mathrm{a}}(1) - V_{\mathrm{a}}(r)) \leq V'_{\mathrm{r},+}(1) \leq V'_{\mathrm{r},+}(\ell(\theta, s, r_2)) \leq V'_{\mathrm{r},+}(\ell(\theta, s, r_2))\partial_{r_1}\ell(\theta, s, r_2).$$

By integration from 1 to r in the variable s we get

$$\frac{1}{2}\left(V_{\mathrm{a}}(1) - V_{\mathrm{a}}(r)\right) \leq \frac{1}{4}\int_1^r V'_{\mathrm{r},+}(\ell(\theta, s, r_2))\partial_{r_1}\ell(\theta, s, r_2)\mathrm{d}s = \frac{1}{4}V_{\mathrm{r}}(\ell(\theta, r, r_2)) - \frac{1}{4}V_{\mathrm{r}}(\ell(\theta, 1, r_2)).$$

By applying this estimate in the second as well as in the third component of $\ell(\theta, r_1, r_2)$ with r_1 and r_2 respectively, we derive

$$V_{\mathrm{a}}(1) + \frac{1}{4}V_{\mathrm{r}}(\ell(\theta, 1, 1)) \leq \frac{1}{2}\left(V_{\mathrm{a}}(r_1) + V_{\mathrm{a}}(r_2)\right) + \frac{1}{4}V_{\mathrm{r}}(\ell(\theta, r_1, r_2)). \tag{A.10}$$

Now for all 2-bonded x_i, using (A.10) with r_i^1, r_i^2, and θ_i, we have

$$\frac{1}{2}\big(V_{\mathrm{a}}(r_i^1) + V_{\mathrm{a}}(r_i^2)\big) + \frac{1}{4}V_{\mathrm{r}}(\ell(\theta_i, r_i^1, r_i^2)) \geq V_{\mathrm{a}}(1) + \frac{1}{4}V_{\mathrm{r}}(\ell(\theta_i, 1, 1)). \tag{A.11}$$

For all 3-bonded x_i, using (A.10) twice, we get

$$\begin{aligned}
\frac{1}{2}\left(V_{\mathrm{a}}(r_i^1) + V_{\mathrm{a}}(r_i^3)\right) + \frac{1}{4}V_{\mathrm{r}}(\ell(\theta_i^1, r_i^1, r_i^3)) \geq V_{\mathrm{a}}(1) + \frac{1}{4}V_{\mathrm{r}}(\ell(\theta_i^1, 1, 1)),\\
\frac{1}{2}\left(V_{\mathrm{a}}(r_i^2) + V_{\mathrm{a}}(r_i^3)\right) + \frac{1}{4}V_{\mathrm{r}}(\ell(\theta_i^2, r_i^2, r_i^3)) \geq V_{\mathrm{a}}(1) + \frac{1}{4}V_{\mathrm{r}}(\ell(\theta_i^2, 1, 1)).
\end{aligned} \tag{A.12}$$

Finally, for all 4-bonded x_i, using (A.10) three times, we have

$$\begin{aligned}
\frac{1}{2}\left(V_{\mathrm{a}}(r_i^1) + V_{\mathrm{a}}(r_i^3)\right) + \frac{1}{4}V_{\mathrm{r}}(\ell(\theta_i^1, r_i^1, r_i^3)) \geq V_{\mathrm{a}}(1) + \frac{1}{4}V_{\mathrm{r}}(\ell(\theta_i^1, 1, 1)),\\
\frac{1}{2}\left(V_{\mathrm{a}}(r_i^3) + V_{\mathrm{a}}(r_i^4)\right) + \frac{1}{4}V_{\mathrm{r}}(\ell(\theta_i^2, r_i^3, r_i^4)) \geq V_{\mathrm{a}}(1) + \frac{1}{4}V_{\mathrm{r}}(\ell(\theta_i^2, 1, 1)),\\
\frac{1}{2}\left(V_{\mathrm{a}}(r_i^2) + V_{\mathrm{a}}(r_i^4)\right) + \frac{1}{4}V_{\mathrm{r}}(\ell(\theta_i^3, r_i^2, r_i^4)) \geq V_{\mathrm{a}}(1) + \frac{1}{4}V_{\mathrm{r}}(\ell(\theta_i^3, 1, 1)).
\end{aligned} \tag{A.13}$$

By applying (A.1), (A.7), (A.11)-(A.13), $V_{\rm a}(1)=-1$, and $V_{\rm r}\geq 0$ we obtain

$$\begin{aligned}
\mathcal{R}^{\rm bnd}(C_n) &\geq \sum_{x_i\in I_2}\Big(\frac{1}{2}\big(V_{\rm a}(r_i^1)+V_{\rm a}(r_i^2)\big)+V_{\rm r}(\ell(\theta_i,r_i^1,r_i^2))\Big)\\
&\quad+\sum_{x_i\in I_3}\Big(\frac{1}{2}\big(V_{\rm a}(r_i^1)+V_{\rm a}(r_i^2)+2V_{\rm a}(r_i^3)\big)+\frac{1}{4}\big(V_{\rm r}(\ell(\theta_i^1,r_i^1,r_i^3))+V_{\rm r}(\ell(\theta_i^2,r_i^2,r_i^3))\big)\Big)\\
&\quad+\sum_{x_i\in I_4}\Big(\frac{1}{2}\big(V_{\rm a}(r_i^1)+V_{\rm a}(r_i^2)+2V_{\rm a}(r_i^3)+2V_{\rm a}(r_i^4)\big)\\
&\qquad\qquad+\frac{1}{4}\big(V_{\rm r}(\ell(\theta_i^1,r_i^1,r_i^3))+V_{\rm r}(\ell(\theta_i^2,r_i^3,r_i^4))+V_{\rm r}(\ell(\theta_i^3,r_i^2,r_i^4))\big)\Big)\\
&\geq -(\#I_2+2\#I_3+3\#I_4)\\
&\quad+\frac{1}{4}\Big(\sum_{x_i\in I_2}V_{\rm r}(\ell(\theta_i,1,1))+\sum_{x_i\in I_3}\sum_{j=1}^{2}V_{\rm r}(\ell(\theta_i^j,1,1))+\sum_{x_i\in I_4}\sum_{j=1}^{3}V_{\rm r}(\ell(\theta_i^j,1,1))\Big).
\end{aligned}\tag{A.14}$$

For later purposes, we remark that this inequality is strict if one bond does not have unit length. This follows from the strict inequality in (A.9).

Recall $\delta=(\#I_2+2\#I_3+3\#I_4)/d$ and note that $\ell(\theta,1,1)=2\sin(\theta/2)$ by (A.8). By using $\theta_i=\theta_i^1+\theta_i^2$ for $x_i\in I_3$, $\theta_i=\theta_i^1+\theta_i^2+\theta_i^3$ for $x_i\in I_4$, and (A.14) we obtain

$$\begin{aligned}
\mathcal{R}^{\rm bnd}(C_n)&\geq -\delta d+\frac{1}{4}\Big(\sum_{x_i\in I_2}V_{\rm r}(\ell(\theta_i,1,1))+\sum_{x_i\in I_3}\sum_{j=1,2}V_{\rm r}(\ell(\theta_i^j,1,1))+\sum_{x_i\in I_4}\sum_{j=1}^{3}V_{\rm r}(\ell(\theta_i^j,1,1))\Big)\\
&=-\delta d+\frac{1}{4}\Big(\sum_{x_i\in I_2}V_{\rm r}\Big(2\sin\Big(\frac{\theta_i}{2}\Big)\Big)+\sum_{x_i\in I_3}\sum_{j=1}^{2}V_{\rm r}\Big(2\sin\Big(\frac{\theta_i^j}{2}\Big)\Big)+\sum_{x_i\in I_4}\sum_{j=1}^{3}V_{\rm r}\Big(2\sin\Big(\frac{\theta_i^j}{2}\Big)\Big)\Big).
\end{aligned}$$

This yields the first inequality in (A.2). We note that this inequality is strict if one of the bonds does not have unit length since then (A.14) is strict. The second inequality in (A.2) follows by a convexity argument: since $V_{\rm r}$ is convex and non-increasing by [v], and $\sin(\theta/2)$ is concave for $\theta\in[0,2\pi]$, we observe that $\theta\mapsto V_{\rm r}(2\sin(\frac{\theta}{2}))$ is a convex function for $\theta\in[0,2\pi]$, see [16, Proof of Lemma 5.1] for details. This along with the fact that $\#I_2+2\#I_3+3\#I_4=\delta d$ and

$$\pi(d-2)=\sum_{i=1}^{d}\theta_i=\sum_{x_i\in I_2}\theta_i+\sum_{x_i\in I_3}(\theta_i^1+\theta_i^2)+\sum_{x_i\in I_4}(\theta_i^1+\theta_i^2+\theta_i^4)$$

yields the second inequality in (A.2). This concludes the proof. □

We now proceed with the proof of Lemma 6.3. Let C_n be a connected $q^n_{\rm sat}$-optimal configuration without bridging atoms. Recall the decomposition $X_n=X_n^{a,\rm bulk}\cup\partial X_n^a\cup I_{\rm ac}^{\rm ext}$ introduced in Subsection 6.2. For $2\leq k\leq 4$ we define

$$I_k^{\pm}=\{x_i\in\partial X_n^a: q_i=\pm 1,\ \ \#(\mathcal{N}(x_i)\cap X_n^a)=k\}.$$

Moreover, we set $I^{\pm}=\bigcup_{k=2}^4 I_k^{\pm}$. Note that $I_k=I_k^+\cup I_k^-$, where I_k is given by (6.5). By Lemma 4.3(a)(ii) C_n has alternating charge distribution. Thus, ∂C_n^a is a cycle of even length $d\in 2\mathbb{N}$ and, by Lemma 4.1, there holds $\#I^-=\#I^+=d/2$. We denote the interior angle of the polygon ∂X_n^a at x_i by θ_i. We start with some preliminary properties.

Lemma A.1. *Let $n\geq 6$ and let C_n be a connected $q^n_{\rm sat}$-optimal configuration. Then*

(i) $\#I_4^+=0$.
(ii) *Let $m\geq 4$ be such that $\#I_2+2\#I_3+3\#I_4\leq 2d-m$. Then $2\#I_2^-+\#I_3^-\geq m+\#I_3^+$.*

Proof. Proof of (i). Assume by contradiction that there exists $x_i\in I_4^+$. Since C_n is a $q^n_{\rm sat}$-optimal configuration, all atoms of charge -1 are 4-bonded with bond angles $\frac{\pi}{2}$, see Lemma 4.3(a)(i),(iv). Hence, x_i is contained in four squares and thus not part of ∂X_n^a.

Proof of (ii). As each atom is at most 4-bonded, see (4.1), we have $\#I_2 + \#I_3 + \#I_4 = d$. This along with (i) and the assumption of (ii) shows

$$\#I_4^- + m = \#I_4 + m \leq \#I_2 = \#I_2^+ + \#I_2^-.$$

This implies

$$\begin{aligned} 2\#I_2^- + \#I_3^- &= (\#I_2^- + \#I_3^- - \#I_2^+) + (\#I_2^+ + \#I_2^-) \geq \#I_2^- + \#I_3^- - \#I_2^+ + \#I_4^- + m \\ &= \#I^- + m - \#I_2^+ = \#I^- + m - \#I^+ + \#I_3^+ + \#I_4^+. \end{aligned}$$

Since there holds $\#I^- = \#I^+$ due to alternating charge distribution and $\#I_4^+ = 0$ by property (i), property (ii) follows. □

Proof of Lemma 6.3(a). By Theorem 2.6, Lemma 4.3(a)(i),(ii), and Remark 2.2 there holds $\mathcal{E}(C_n) = -b$. Therefore, $\theta_i \geq (k-1)\frac{\pi}{2}$ if $x_i \in I_k$ by Lemma 4.2(b). This implies

$$\#I_2 + 2\#I_3 + 3\#I_4 \leq \frac{2}{\pi}\sum_{i=1}^{d}\theta_i = 2d - 4,$$

where in the last step we used that the sum of the interior angles equals $\pi(d-2)$. This shows (6.6).

We now show the additional statement. To this end, suppose that $\#\mathcal{A}(X_n) \geq \#\mathcal{A}(X_n^{\mathrm{a,bulk}}) + 2$. We claim that

$$\#\{x_i \in I_2 : \theta_i \geq 5\pi/6\} \geq 2. \tag{A.15}$$

We defer the proof of (A.15) and first conclude the proof of the statement. The fact that the sum of the interior angles equals $\pi(d-2)$ and (A.15) imply

$$1 + \#I_2 + 2\#I_3 + 3\#I_4 < \frac{2}{\pi}\frac{5}{6}\pi \cdot 2 + (\#I_2 - 2) + 2\#I_3 + 3\#I_4 \leq \frac{2}{\pi}\sum_{i=1}^{d}\theta_i = 2d - 4.$$

Since the left and the right hand side are integers, we find $2 + \#I_2 + 2\#I_3 + 3\#I_4 \leq 2d - 4$. This shows that $m \geq 6$ in (6.6). It remains to prove (A.15). As a preparation, we first show that

$$x \in \mathcal{A}(X_n) \quad \Rightarrow \quad x \in X^+,\ x \text{ is 2-bonded and bond-angles at } x \text{ lie in } [5\pi/6, 7\pi/6]. \tag{A.16}$$

By Lemma 4.3(a)(i),(iv),(v) we observe that x is 2-bonded and has charge $+1$. Denote the two neighbors of $x \in \mathcal{A}(X_n)$ by z_1 and z_2. Since z_1 and z_2 have charge -1, they are 4-bonded. Also note that $(\mathcal{N}(z_1) \cap \mathcal{N}(z_2)) \setminus \{x\} = \emptyset$. In fact, if there was an atom $y \in (\mathcal{N}(z_1) \cap \mathcal{N}(z_2)) \setminus \{x\}$, the four atoms z_1, x, z_2, and y would form a square. Due to Lemma 4.2(b), this square is regular which contradicts the fact that $x \in \mathcal{A}(X_n)$. Now, if we had that a bond-angle at x does not lie in $[5\pi/6, 7\pi/6]$, it is elementary to see that $\mathrm{dist}(\mathcal{N}(z_1) \setminus \{x\}, \mathcal{N}(z_2) \setminus \{x\}) < \sqrt{2}$. This would contradict the fact that C_n is repulsion-free.

We now show that (A.15) holds. Recall the assumption $\#\mathcal{A}(X_n) \geq \#\mathcal{A}(X_n^{\mathrm{a,bulk}}) + 2$. We consider the two cases (a) $\mathcal{A}(X_n) \cap \partial X_n^{\mathrm{a}} \neq \emptyset$ and (b) $\mathcal{A}(X_n) \cap \partial X_n^{\mathrm{a}} = \emptyset$.

Proof of Case (a). Observe that $\#(\partial X_n^a \cap \mathcal{A}(X_n)) \geq 2$ by Lemma 4.2(a). Additionally, by (A.16) we get $\partial X_n^a \cap \mathcal{A}(X_n) \subset I_2^+$ and $\theta_i \geq 5\pi/6$ for $x_i \in \partial X_n^a \cap \mathcal{A}(X_n)$. Hence, (A.15) holds.

Proof of Case (b). We first show that for each $x \in \mathcal{A}(X_n) \setminus \mathcal{A}(X_n^{\mathrm{a,bulk}})$ we can find

$$z_x \in X_n \quad \text{such that } z_x \in I_2^+,\ |x - z_x| = \sqrt{2},\ \text{and the two bond-angles at } z_x \text{ equal } \pi. \tag{A.17}$$

By (A.16) we get that $x \in X_n^+$, that it is 2-bonded in X_n and, since $x \in \mathcal{A}(X_n) \setminus \mathcal{A}(X_n^{\mathrm{a,bulk}})$, it is 1-bonded in $X_n^{\mathrm{a,bulk}}$. Thus, there exists exactly one atom in $\mathcal{N}(x) \cap \partial X_n^{\mathrm{a}}$, denoted by x_i. By x_{i-1}, x_{i+1} we denote the two neighbors of x_i in $\partial X_n^{\mathrm{a}}$. At least one of these two atoms, say without restriction x_{i-1}, satisfies $|x_{i-1} - x| = \sqrt{2}$, see Fig. 13. We will identify x_{i-1} as the atom z_x in (A.17). Recall the assumption $\partial X_n^a \cap \mathcal{A}(X_n) = \emptyset$, which implies that the bond-angles at x_{i-1} lie in $\{\pi/2, \pi, 3\pi/2\}$. Let $y \in \mathcal{N}(x_{i-1}) \setminus \{x_i\}$. Suppose y, x_i, and x_{i-1} would form an angle in $\{\pi/2, 3\pi/2\}$, i.e., $|y - x_i| = \sqrt{2}$. Then either (i) x_{i-1}, y, x, x_i or (ii) x_{i-1}, y, z, x_i form a square, where $z \in \mathcal{N}(x_i) \setminus \{x, x_{i-1}\}$, see Fig. 13. In view of (A.16), case (i) contradicts $x \in \mathcal{A}(X_n)$, and case (ii) contradicts $x_{i-1} \in \partial X_n^{\mathrm{a}}$. This shows that y, x_{i-1}, x_i form an angle π, and this also yields that $x_{i-1} \in I_2^+$. We denote x_{i-1} by z_x.

Since $\#\mathcal{A}(X_n) \geq \#\mathcal{A}(X_n^{\mathrm{a,bulk}}) + 2$ by assumption, we find $x \neq y \in \mathcal{A}(X_n) \setminus \mathcal{A}(X_n^{\mathrm{a,bulk}})$. We now show that $z_x \neq z_y$, where z_x and z_y are the atoms identified in (A.17). This will imply (A.15). Assume by contradiction that $z_x = z_y$. Denote $z_x = z_y$ by $x_i \in I_2^+$ and recall $\theta_i = \pi$. Denote its two neighbors by x_{i-1}, x_{i+1}, and recall that they are 4-bonded, in particular bonded to x or y, respectively. Consider the unique atoms $w_x \in \mathcal{N}(x) \setminus \partial X_n^{\mathrm{a}}$ and $w_y \in \mathcal{N}(y) \setminus \partial X_n^{\mathrm{a}}$. Observe that they are 4-bonded. First, note that $\mathcal{N}(w_x) \cap \mathcal{N}(w_y) = \emptyset$ since the contrary would imply that x, y would be contained in an octagon with bond angles $\pi, \pi/2$ respectively, contradicting the fact that $x, y \in \mathcal{A}(X_n)$. Since by (A.16) the bond angles at $x, y \in \mathcal{A}(X_n)$ lie in $[5\pi/6, 7\pi/6]$, an elementary argument shows that $\mathrm{dist}(\mathcal{N}(w_x), \mathcal{N}(w_y)) < \sqrt{2}$, see Fig. 13. This contradicts the fact that C_n is repulsion-free and concludes the proof of case (b). □

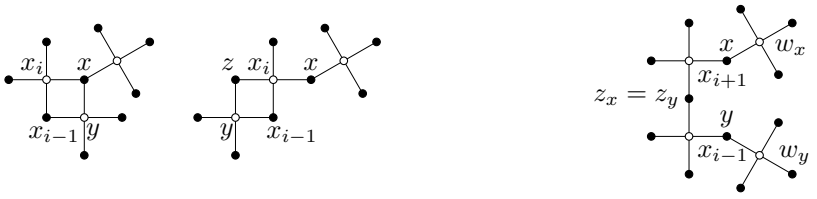

FIGURE 13. The relevant parts of the configurations considered in the proof of Case (b). Left: The two cases (i) and (ii) in the proof of (A.17). Right: The situation $z_x = z_y$.

Proof of Lemma 6.3(b). We proceed in several steps. We first introduce an auxiliary configuration C'_{n-d} which arises from C_n by removing the boundary and adding again the 3-bonded boundary atoms of charge +1 (Step 1). We collect some properties about the net charge of C'_{n-d} whose proofs are deferred to Steps 3 and 4. In Step 2 we define the configuration C_{n-d-m} by suitably adding atoms of charge +1 to C'_{n-d}, and we prove the statement of the lemma.

Step 1: An auxiliary configuration. We recall the decomposition $X_n = X_n^{a,\mathrm{bulk}} \cup \partial X_n^a \cup I_{\mathrm{ac}}^{\mathrm{ext}}$ introduced in Subsection 6.2. By Lemma 4.2(a) and Lemma 4.1, ∂C_n^a is a cycle of even length d with alternating charge distribution, and therefore $\mathcal{Q}(\partial C_n^a) = 0$. Moreover, all exterior acyclic bonds have charge +1. This implies

$$\mathcal{Q}(C_n) = \mathcal{Q}(C_n^{a,\mathrm{bulk}}) + \mathcal{Q}(\partial C_n^a) + \mathcal{Q}(I_{\mathrm{ac}}^{\mathrm{ext}}) = \mathcal{Q}(C_n^{a,\mathrm{bulk}}) + \#I_{\mathrm{ac}}^{\mathrm{ext}}. \tag{A.18}$$

We introduce an auxiliary configuration C'_{n-d} by

$$C'_{n-d} = C_n^{a,\mathrm{bulk}} \cup \bigcup\nolimits_{x_i \in I_3^+} (x_i, 1). \tag{A.19}$$

In a similar fashion, we denote the atomic positions by X'_{n-d}. It is clear that $\mathcal{Q}(C'_{n-d}) = \mathcal{Q}(C_n^{a,\mathrm{bulk}}) + \#I_3^+$. By construction there holds $\mathcal{A}(X_n^{\mathrm{a,bulk}}) = \mathcal{A}(X'_{n-d})$ since all the atoms added from I_3^+ are 1-bonded in C'_{n-d}, more precisely, bonded to an atom which does not lie in $\mathcal{A}(X_n)$. By (A.18) we get

$$\mathcal{Q}(C_n) = \mathcal{Q}(C'_{n-d}) + \#I_{\mathrm{ac}}^{\mathrm{ext}} - \#I_3^+. \tag{A.20}$$

The goal is to estimate the contributions of the different terms in (A.20) separately: we will show that

$$\mathcal{Q}(C'_{n-d}) \geq \phi\big(n - d - (\#I_{\mathrm{ac}}^{\mathrm{ext}} - \#I_3^+)\big), \tag{A.21}$$

$$\#I_{\mathrm{ac}}^{\mathrm{ext}} - \#I_3^+ \geq m, \tag{A.22}$$

where $m \geq 4$ is given in (6.6). We defer the proof of (A.21)–(A.22) to Steps 3 and 4 below and proceed to show the statement of the lemma.

Step 2: Proof of the statement: First, (A.22) implies $\#I_{\mathrm{ac}}^{\mathrm{ext}} \geq \#I_3^+ + m \geq m$. Next, we construct the configuration C_{n-d-m}. A difficulty arises from the fact that the auxiliary configuration C'_{n-d} possibly does not satisfy the net charge equality (6.7) and therefore we need to add atoms of charge +1.

We set $k_m := \#I_{\mathrm{ac}}^{\mathrm{ext}} - \#I_3^+ - m$ and observe that $k_m \geq 0$ by (A.22). We define

$$C_{n-d-m} := C'_{n-d} \cup \big\{(z_1, 1), \dots, (z_{k_m}, 1)\big\},$$

where the positions are chosen such that $\min\{\mathrm{dist}(z_i, X_n), \mathrm{dist}(z_i, z_j) : i \neq j\} \geq \sqrt{2}$. In view of (A.19), we observe that C_{n-d-m} indeed consists of

$$n - d - \#I_{\mathrm{ac}}^{\mathrm{ext}} + \#I_3^+ + k_m = n - d - \#I_{\mathrm{ac}}^{\mathrm{ext}} + \#I_3^+ + \#I_{\mathrm{ac}}^{\mathrm{ext}} - \#I_3^+ - m = n - d - m$$

atoms. Since the added atoms are all 0-bonded, in view of (A.19), X_{n-d-m} is a subset of X_n up to 0-bonded atoms. Moreover, we clearly have $\mathcal{A}(X_{n-d-m}) = \mathcal{A}(X'_{n-d})$ and thus $\mathcal{A}(X_{n-d-m}) = \mathcal{A}(X_n^{\mathrm{a,bulk}})$. As we have added k_m 0-bonded atoms of charge $+1$ to C'_{n-d}, C_{n-d-m} still satisfies Lemma 4.3(a)(i),(ii), and thus by Lemma 4.3(b) there holds equality in (4.5). Therefore, C_{n-d-m} is optimal and satisfies $\mathcal{Q}(C_{n-d-m}) \geq q_{\mathrm{sat}}^{n-d-m}$ by Lemma 4.3(a)(iii). Moreover, we clearly have $\mathcal{Q}(C_{n-d-m}) = \mathcal{Q}(C'_{n-d}) + k_m$. By (A.20) and the definition $k_m = \#I_{\mathrm{ac}}^{\mathrm{ext}} - \#I_3^+ - m$ we observe

$$\mathcal{Q}(C_n) = \mathcal{Q}(C'_{n-d}) + \#I_{\mathrm{ac}}^{\mathrm{ext}} - \#I_3^+ = \mathcal{Q}(C_{n-d-m}) + \#I_{\mathrm{ac}}^{\mathrm{ext}} - k_m - \#I_3^+ = \mathcal{Q}(C_{n-d-m}) + m.$$

This shows (6.7) and concludes the proof of the statement. To conclude the proof, it thus remains to show (A.21) and (A.22).

Step 3: Proof of (A.21). We first recall that $C_n^{a,\mathrm{bulk}}$ consists of $n - d - \#I_{\mathrm{ac}}^{\mathrm{ext}}$ atoms and thus C'_{n-d} consists of $\#X'_{n-d} := n - d - (\#I_{\mathrm{ac}}^{\mathrm{ext}} - \#I_3^+)$ atoms. Thus, in view of Lemma 4.3(a)(iii) it suffices to prove

$$\mathcal{E}(C'_{n-d}) = -2\#X'_{n-d} + 2\mathcal{Q}(C'_{n-d}). \tag{A.23}$$

By Lemma 4.3(a)(i),(ii) we find that C_n is repulsion-free with unit bond lengths and all atoms of charge -1 are 4-bonded. Since $C'_{n-d} \subset C_n$, also C'_{n-d} is repulsion-free with unit bond lengths. We now show that each atom of C'_{n-d} with charge -1 is 4-bonded. Let $x_i \in X'_{n-d}$ with $q_i = -1$. We first show that $\mathcal{N}(x_i) \cap (X_n \setminus X'_{n-d}) = \emptyset$. In fact, in view of (A.19) and $q_i = -1$, we have

$$\mathcal{N}(x_i) \cap (X_n \setminus X'_{n-d}) \subset (\partial X_n^a \setminus I_3^+) \cap X_n^+ = I_2^+ \cup I_4^+. \tag{A.24}$$

We first recall that $\#I_4^+ = \emptyset$, see Lemma A.1(i). Moreover, atoms in $\mathcal{N}(x_i) \cap (X_n \setminus X'_{n-d})$ cannot lie in I_2 since atoms in I_2 are only bonded to other atoms in ∂X_n^a or to atoms in $I_{\mathrm{ac}}^{\mathrm{ext}}$, see (6.5). Then (A.24) shows $\mathcal{N}(x_i) \cap (X_n \setminus X'_{n-d}) = \emptyset$.

This implies that the neighborhood of x_i in X'_{n-d} coincides with the one in X_n, and thus x_i is still 4-bonded, cf. Lemma 4.3(a)(i). Consequently, we have shown that C'_{n-d} satisfies Lemma 4.3(a)(i),(ii). Then (A.23) follows from Lemma 4.3(b).

Step 4: Proof of (A.22). Since $n \geq 6$ and C_n does not contain bridging atoms, we can apply Lemma 6.1(b). We get that $I_{\mathrm{ac}}^{\mathrm{ext}} = I_{\mathrm{ac}}^{\mathrm{ext}} \cap X_n^+$ and that each atom in $I_{\mathrm{ac}}^{\mathrm{ext}}$ is 1-bonded. For all $x_i \in I_3^-$ there exists exactly one $x_j \in \mathcal{N}(x_i) \cap I_{\mathrm{ac}}^{\mathrm{ext}}$, whereas for $x_i \in I_2^-$ there exist exactly two $x_j, x_k \in \mathcal{N}(x_i) \cap I_{\mathrm{ac}}^{\mathrm{ext}}$. As atoms in $I_{\mathrm{ac}}^{\mathrm{ext}}$ are 1-bonded, it is clear that no atom in $I_{\mathrm{ac}}^{\mathrm{ext}}$ is bonded to two different atoms in $I_2^- \cup I_3^-$. This yields

$$\#I_{\mathrm{ac}}^{\mathrm{ext}} \geq 2\#I_2^- + \#I_3^-.$$

Then (A.22) follows from (6.6) and Lemma A.1(ii). □

Acknowledgements

This work was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy EXC 2044 -390685587, Mathematics Münster: Dynamics–Geometry–Structure.

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