Finite crystallization in the square lattice

2014 Nonlinearity 27 717

(http://iopscience.iop.org/0951-7715/27/4/717)

IOP Publishing | London Mathematical Society Nonlinearity

Nonlinearity **27** (2014) 717–737 doi:10.1088/0951-7715/27/4/717

Finite crystallization in the square lattice

Edoardo Mainini[1], Paolo Piovano[2,3] and Ulisse Stefanelli[2,3]

[1] Università degli Studi di Genova, Dipartimento di Ingegneria meccanica, energetica, gestionale e dei trasporti (DIME)-sezione MAT, Piazzale Kennedy 1, I-16129 Genova, Italy
[2] Istituto di Matematica Applicata e Tecnologie Informatiche 'E Magenes'-CNR, via Ferrata 1, I-27100 Pavia, Italy
[3] Faculty of Mathematics, University of Vienna, Oskar-Morgenstern-Platz 1, A-1090 Vienna, Austria

Received 5 December 2013
Accepted for publication 30 January 2014
Published 21 March 2014

Recommended by C Le Bris

Abstract
This paper addresses two-dimensional crystallization in the square lattice. A suitable configurational potential featuring both two- and three-body short-ranged particle interactions is considered. We prove that every ground state is a connected subset of the square lattice. Moreover, we discuss the global geometry of ground states and their optimality in terms of discrete isoperimetric inequalities on the square graph. Eventually, we study the aspect ratio of ground states and quantitatively prove the emergence of a square macroscopic Wulff shape as the number of particles grows.

Keywords: crystallization, square lattice, atomic interaction potentials, boundary energy, edge isoperimetric inequality

Mathematics Subject Classification: 82D25

1. Introduction

The understanding of the crystallization process in solids is of paramount importance in both theoretical and applied situations. However, there have been only a few rigorous mathematical results regarding crystallization. In this paper, we present a comprehensive analysis of the crystallization of a *finite* number of particles in the two-dimensional square lattice.

At very low temperature, atomic interactions are expected to be governed solely by the respective positions of particles. Configurations are identified with the particle positions $\{x_1, \ldots, x_n\} \in \mathbb{R}^2$ and we are concerned with the minimization of the interaction energy $E : \mathbb{R}^{2n} \to \mathbb{R} \cup \{+\infty\}$. The crystallization problem consists of characterizing the local and global geometry of ground-state configurations of E. More precisely, crystallization occurs when ground states of E are periodic.

The energy E is here assumed to decompose as $E = E_2 + E_3$ where E_2 and E_3 respectively describe two- and three-body interactions. The two-body interaction potential E_2 is short-ranged and attractive–repulsive. While E_2 favours particles sitting at some specific positive interatomic distance, E_3 encodes three-body interactions by favouring triples of particles forming $\pi/2$ and π bond angles. Under suitable qualifications, specified in section 2, we prove that finite-particle minimizers of E are subsets of the square lattice (sections 3, 4 and 5). In particular, note that E_3 needs to satisfy non-degeneracy assumptions at minimizers.

Furthermore, we exactly quantify the ground-state energy in terms of the number of particles. This quantification has a number of consequences as it determines explicitly the global geometry of ground states. In particular, it provides a complete description of the surface-tension effect as well as a striking tool towards uniqueness, or rather generic nonuniqueness, of ground states (section 6). As the energy E favours particle bonding and 'boundary' particles necessarily have fewer bonds, ground states can be intuitively expected to have minimal perimeter, or maximal area. This intuition is made rigorous in section 7, upon noting that ground states can be characterized as those configurations which realize equality in a discrete isoperimetric inequality. Additionally, we explicitly compute the exact values of ground-state perimeter and area in terms of the number of particles.

Finally, in section 8 we prove that ground states converge in a precise quantitative way to a square as the number of particles grows. In particular, the emergence of a macroscopic Wulff shape in the large-particle limit is shown. This result nicely reflects the inherent multiscale nature of the crystallization phenomenon.

To the best of our knowledge this paper represents the first rigorous crystallization results for the square system. In view of applications, this is of course a quite relevant crystallization setting. For the sake of putting our contribution into perspective, we shall propose here a minimal crystallization literature overview. The reader is referred instead to Le Bris and Lions [14] for a more general perspective.

In the one-dimensional case, crystallization under Lennard-Jones pair interactions $E = E_2$ was first proved by Gardner and Radin in [8]. Since then, a number of results have emerged, showing, whether or not, with different choices of E_2, the stability (under perturbations) and the minimality properties apply to the configuration of equally spaced particles. We quote in particular [9, 18, 21] as well as the more recent [3] where a one-dimensional crystallization problem is addressed in a quantum-mechanical setting.

The first crystallization result in the two-dimensional triangular lattice was established by Heitmann and Radin in [13] for highly symmetric and singular interactions. More precisely, in [13] the authors considered the crystallization of an ensemble of hard discs which maximize relative tangencies (see also [11]). In [16] and [22] the results were refined for first-neighbour interacting soft discs which allow interaction at distance and have been extended to quasicrystals in [17]. Instead, the emergence of a macroscopic Wulff shape for short-range two-body interaction potentials has recently been investigated in [24]. With respect to these contributions, the novelty of our results consists not only of concentrating on a different crystalline structure by exploiting three-body interactions, but more relevantly in explicitly quantifying the ground-state and surface energies and relating ground states with perimeter and area extremality. In this respect, our results in section 7 on isoperimetric inequalities on the square graph are closely related to some classical issue in discrete mathematics, see [4, 10]. As a consequence of our analysis an explicit quantification of the optimal area and perimeter is provided.

In [15] another short-range interaction including a three-body term is considered, the E_3 part being modelled on the geometry of sp^2-covalent bonding of carbon atoms, favouring $2\pi/3$ angles between carbon–carbon bonds. Still, an explicit characterization of ground-state energy is provided therein and ground states are shown to be subsets of the hexagonal lattice (graphene) which suitably minimize their boundary length. With respect to the hexagonal setting of [15], our results for the square system provide a more comprehensive description of the global geometry of ground states as well as the macroscopic large-particle shape.

As far as long-range interactions are considered in two dimensions, the first crystallization result is due to Theil (see [20]), the interactions being governed by a Lennard-Jones-like two-body potential. This case is considerably more involved since the effect of long-range interaction needs to be controlled by means of a specific localization technique. In [20], an *infinite* crystallization problem is considered in its *thermodynamic limit*, and it is proved that the energy of ground states converges to the energy density of a (suitably rescaled) copy of the regular triangular lattice as the number of particles tends to infinity. Moreover, by imposing suitable periodic or well-prepared Dirichlet conditions, Theil proved that ground states necessarily correspond to subsets of the regular triangular lattice. Some seminal numerical illustration of two-dimensional crystallization can be found in [23]. The result by Theil has then been reconsidered in [5] by including a three-body interaction term which favours $2\pi/3$ angles, so that one expects crystallization in the hexagonal lattice instead of the triangular one. In [5] the authors establish the thermodynamic limit and the hexagonal crystallization under periodic Dirichlet conditions.

Regarding rigorous crystallization results in three dimensions, the purely two-body case $E = E_2$ is still open although the natural candidate ground states are the *face-centred cubic* (fcc) and the *hexagonally close-packed* (hcp) lattices. The reader is referred to [7] for some convincing evidence in this direction. The only available result in three dimensions asks for an additional E_3 three-body term favouring $\pi/3$ bonds: the recent paper [6] extends to three dimensions the analysis of [20]. In particular, the authors quantify the thermodynamic limit of the energy density of ground states that corresponds to a suitably rescaled fcc-lattice and prove that ground states are actually fcc-lattice subsets under suitable boundary conditions. However, by letting E_3 favour $2\pi/3$ and $4\pi/3$ bonds, in [15] it is proved that finite ground states need necessarily to be nonplanar. Furthermore, it is shown in [15] that rolled-up structures like nanotubes are energetically favourable and that the classical C_{20} and C_{60} fullerenes are local energy minimizers.

2. Energy and elementary properties of configurations

A *configuration* of n identical particles will be indicated by C_n and identified with the respective particle positions $\{x_1, \cdots, x_n\} \in \mathbb{R}^{2n}$. We denote by ℓ_{ij} the distance between two particles x_i and x_j, and by θ_{ijk} the angle determined by the two segments $x_i - x_j$ and $x_k - x_j$ (the choice of the angle orientation being inconsequential) (figure 1).

The energy $E = E(C_n)$ of a configuration C_n is given by

$$E(C_n) := \frac{1}{2}\sum_{i\neq j} E_2(\ell_{ij}) + \frac{1}{2}\sum_{(i,j,k)\in\mathcal{A}} E_3(\theta_{ijk}), \tag{1}$$

where the functions $E_2 : [0,\infty) \to [-1,\infty]$ and $E_3 : [0, 2\pi] \to [0,\infty)$ are, respectively, the two-body and the three-body interaction potentials. We choose a strongly repulsive, short-ranged two-body potential E_2 in the form

$$E_2(\ell) := \begin{cases} +\infty & \text{if } \ell < 1, \\ -1 & \text{if } \ell = 1, \\ v(\ell) & \text{if } 1 < \ell < \ell^*, \\ 0 & \text{if } \ell \geqslant \ell^*, \end{cases} \tag{2}$$

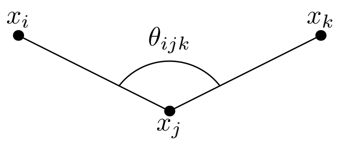

Figure 1. Notation for bonds and bond angles.

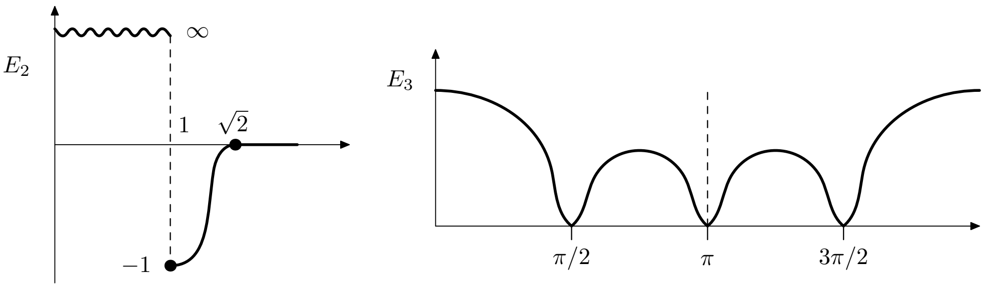

Figure 2. The interaction functions E_2 and E_3.

where v is any function taking its values in $(-1, 0)$ and $\ell^* \in (1, \sqrt{2})$ is a given number (figure 2). On the other hand, let σ be some constant in $(0, \pi/8)$ and define

$$I_1 := \left[\frac{\pi}{2} - \sigma, \frac{\pi}{2} + \sigma\right], \quad I_2 := [\pi - \sigma, \pi + \sigma], \quad I_3 := \left[\frac{3\pi}{2} - \sigma, \frac{3\pi}{2} + \sigma\right],$$
$$I := I_1 \cup I_2 \cup I_3. \tag{3}$$

The three-body potential E_3 is assumed to vanish only at $\pi/2$, π, and $3\pi/2$, symmetric with respect to π (which motivates the factor $1/2$ in front of the three-body energy term), convex in I_1, and to satisfy the following non-degeneracy and symmetry conditions:

$$E_3(\theta) > 8 \quad \text{if } \theta \in \left(\theta_{\min}, \frac{2\pi}{5}\right], \tag{4a}$$

$$E_3(\theta) > 4 \quad \text{if } \theta \notin I, \tag{4b}$$

$$E_3(\theta) = E_3(\theta + \frac{\pi}{2}) = E_3(\theta + \pi) \quad \text{if } \theta \in I_1, \tag{4c}$$

$$E'_{3,-}\left(\frac{\pi}{2}\right) := \lim_{t \nearrow 0} \frac{1}{t} E_3(t+\pi/2) < -\frac{2}{\pi}. \tag{4d}$$

We say that two particles x_i and x_j are *bonded* or that there is an (*active*) *bond* between x_i and x_j, if $1 \leqslant \ell_{ij} < \ell^*$. This particularly entails that $E_2(\ell_{ij})$ is negative. The set $\mathcal{A}$ appearing in the second sum in (1) is defined as the set of all triples (i, j, k) for which the angle θ_{ijk} separates two active bonds. The angle θ_{ijk} is said to be a (*active*) *bond angle* if $(i, j, k) \in \mathcal{A}$. Note that the hard-interaction assumption $E_2 = \infty$ on $(0, 1)$ can be relaxed by making E_2 very large in a left neighbourhood of 1 (see [5, 20, 24]).

The set of vertices and line segments corresponding to active bonds forms a graph which we call a *bond graph*. In the following, we often identify configurations with the respective bond graph, and use equivalently the terms *particle* or *vertex*, and *bond* or *edge*. It is worth noting that, as $E_2(\ell)$ vanishes for $\ell \geqslant \sqrt{2}$, the bond graph is necessarily *planar*. Indeed, given a quadrilateral with all sides and one diagonal in $[1, \sqrt{2})$, the second diagonal is at

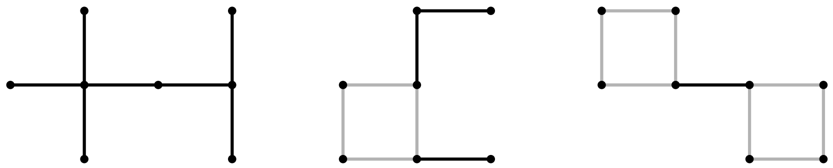

Figure 3. Examples of *flags* (bold in the first two) and a *bridge* (bold in the last picture).

least $\sqrt{2}$. In particular, all interactions are restricted to *nearest neighbours* only. Additionally, one can use definition (2) and check that the minimal angle between two active bonds is $\theta_{\min} := 2\arcsin(1/(2\sqrt{2})) \approx 0.23\,\pi$ for all finite-energy configurations.

We recall that the bond graph is said to be *connected* if each two vertices are joinable by a simple path. In this case, by a slight abuse of terminology, we will also say that the corresponding configuration is connected. As all bonds are line segments, every simple cycle in the bond graph is a *polygon* (note that, possibly, some internal angles of a polygon may be equal to π). Let us term *acyclic* all bonds which do not belong to any polygon. Among these we distinguish between *flags* and *bridges*. A *bridge* is an acyclic bond contained in some simple path connecting two particles that belong to distinct polygons. *Flags* are instead all other acyclic bonds, see figure 3.

In the following, we will often refer to the *removal* of a given bonded particle x from an n-particles configuration. By this we mean that we consider *another* n-particles configuration such that the particle x is relocated so far away that it has no active bonds. Observe that an acyclic bond univocally identifies two maximal (by set inclusion), distinct connected subconfigurations (each containing one and only one of the vertices of that bond). By *removal* of the acyclic bond we mean that we consider another configuration where these subconfigurations are rigidly moved sufficiently far apart so that such bond is deactivated. Moreover, each flag can be considered as corresponding to a single particle. In particular, if a configuration has f flags one may *remove* the f flag-bonds by *removing* exactly f particles.

In order to introduce the notion of *defect*, we define an *elementary polygon* of a configuration as a simple cycle with no bonds in its interior region. A defect is an elementary polygon with more than four bonds. We say that a configuration is *defect-free* if it has no defects.

The aim of this paper is to investigate the global minimizers of the energy E, for any fixed $n \in \mathbb{N}$. We shall term these global minimizers *ground states*. Note that ground states exist for every $n \in \mathbb{N}$. Indeed, E is continuous and the ground-state energy is clearly negative (for all $n > 1$). Hence, all ground states are necessarily contained in a sufficiently large ball (if particles are too far apart, no bonds are active and we have $E = 0$). This proves the coercivity of E. As the energy is clearly rotation and translation invariant, we shall tacitly assume in all of the following that statements are to be considered up to isometries.

We refer to $\mathbb{Z}^2$ as the *square lattice* and to the graph binding nearest neighbours in $\mathbb{Z}^2$ as the *square graph*. A configuration is said to be *square* if it is a subset of $\mathbb{Z}^2$ and its bond graph is a subset of the square graph. Given a square configuration C_n we define its z-row and z-column by

$$C_n(\cdot, z) := \{(p, q) \in C_n : q = z\} \qquad \text{and} \qquad C_n(z, \cdot) := \{(p, q) \in C_n : p = z\} \tag{5}$$

for every $z \in \mathbb{Z}$. A square configuration C_n is defined to be *convex by rows and columns* if for every $z \in \mathbb{Z}$ both the bond graph of the row $C_n(\cdot, z)$ and the bond graph of the column $C_n(z, \cdot)$ of C_n are connected. In particular, we have that a square configuration C_n that is convex by rows and columns is defect-free.

We also introduce the class of *regular* configurations, thought of as small distortions of square ones. We say that a configuration is *regular* if each of its particles has at most four bonds, each of the polygons in its bond graph has at least four edges, and all the bond angles are in I. The relevance of this concept is clarified by the following elementary result.

Proposition 2.1. *All ground states are regular.*

Proof. Since the minimum bond angle $\theta_{\min}$ is greater than $2\pi/9$, the number of bonds of ground-state particles needs to be less than nine. The case of a particle x with a number of bonds between five and eight is excluded by hypothesis (4*a*) since the energy would strictly decrease by removing x. Moreover, every polygon in a ground state has at least 4 edges from (4*a*). In fact, if a bond graph of a ground state contains a triangle, then this will have an internal angle which is smaller or equal to $\pi/3$. Therefore, again in view of (4*a*), we can find a configuration with strictly lower energy by removing the particle associated to that angle. This contradicts the fact that the bond graph of a ground state contains a triangle. Analogously, the fact that all the bond angles of a ground state need to be in I follows directly from hypothesis (4*b*). □

Finally, denoting by $b = b(C_n)$ the number of bonds in the bond graph of a given configuration C_n, it is straightforward to check the lower energy bound

$$E \geqslant -b. \tag{6}$$

Indeed, (6) follows from the fact that $E_3 \geqslant 0$ and $E_2 \geqslant -1$. In particular, equality holds in (6) if and only if C_n is square. We conclude that the energy of square configurations can be computed by simply counting the number of bonds. Additionally, let us remark that defects in square configurations necessarily have at least eight bonds.

3. Boundary energy

Given a configuration C_n, we say that $x \in C_n$ is a *boundary particle* if it is not contained in the interior region of any polygon of the bond graph, and we call a bond connecting two boundary particles a *boundary bond*. In the following, we denote by $d = d(C_n)$ the number of boundary particles of C_n. Accordingly, the remaining $n - d$ vertices will be addressed as *interior* vertices. Furthermore, we define the *bulk configuration* C_n^{bulk} as the configuration consisting of all the $n - d$ interior vertices of C_n and denote by $E^{\mathrm{bulk}} = E^{\mathrm{bulk}}(C_n)$ the energy (1) corresponding to C_n^{bulk}. Moreover, we call *boundary energy* $E^{\mathrm{bnd}} = E^{\mathrm{bnd}}(C_n)$ the function defined by

$$E^{\mathrm{bnd}}(C_n) := E(C_n) - E^{\mathrm{bulk}}(C_n) = E(C_n) - E(C_n^{\mathrm{bulk}}). \tag{7}$$

In addition, we denote by $\Gamma = \Gamma(C_n)$ and by $\Theta = \Theta(C_n)$, respectively, the set of all bonds and the set of all bond angles which are deactivated in C_n by *removing* boundary particles. We stress that some of the angles in $\Theta(C_n)$ may be adjacent to *interior* vertices of C_n. In the following we will often omit the dependence of these objects on the configuration C_n being considered, when no ambiguity arises.

Since $E_2 \geqslant -1$ we observe that E^{bnd} satisfies

$$E^{\mathrm{bnd}} \geqslant -\#\Gamma + \sum_{\theta_i \in \Theta} E_3(\theta_i) \tag{8}$$

and the latter holds with an equality if (and not only if) the configuration is square. In such case E^{bnd} equals the cardinality of Γ up to sign.

The following lemma provides the crucial estimate on E^{bnd}.

Lemma 3.1. *Let $n \geqslant 4$ and let C_n be a connected regular configuration without flags and bridges. Then,*

$$E^{\mathrm{bnd}} \geqslant -2d + 4. \tag{9}$$

Proof. Since C_n is connected and does not have any flags or bridges, its bond graph contains a *boundary polygon*, made by the d boundary particles and the bonds between them, and containing all the other $n-d$ particles in its interior region. In the following, we will denote the boundary polygon by P_d. Furthermore, since C_n is also regular, all the internal angles of P_d need to be in I, the set defined in (3). Let ε, η, and ν be the ratios of the internal angles of P_d that belong to I_1, I_2, and I_3, respectively. Furthermore, we denote by φ_i, for $i = 1, \ldots, \varepsilon d$, the internal angles of P_d that are in I_1, by ψ_i, for $i = 1, \ldots, \eta d$, the internal angles of P_d in I_2, and by ξ_i, for $i = 1, \ldots, \nu d$, the internal angles of P_d in I_3.

Since the sum of the internal angles of a polygon with d sides is $\pi(d-2)$, we observe that

$$\varepsilon\, d\varphi + \eta\, d\psi + \nu\, d\xi = \pi(d-2), \tag{10}$$

where

$$\varphi := \frac{1}{\varepsilon d}\sum_{i=1}^{\varepsilon d}\varphi_i, \qquad \psi := \frac{1}{\eta d}\sum_{i=1}^{\eta d}\psi_i \qquad \text{and} \quad \xi := \frac{1}{\nu d}\sum_{i=1}^{\nu d}\xi_i.$$

Furthermore, by (4*c*) and by the convexity of E_3 in I_1 we have that

$$E_3(\psi_i) = E_3\left(\psi_i - \frac{\pi}{2}\right) + E_3\left(\frac{\pi}{2}\right) \geqslant 2E_3\left(\frac{\psi_i}{2}\right) \tag{11}$$

for every $i = 1, \cdots, \eta d$, and

$$E_3(\xi_i) = E_3\left(\xi_i - \pi\right) + E_3\left(\frac{\pi}{2}\right) + E_3\left(\frac{\pi}{2}\right) \geqslant 3E_3\left(\frac{\xi_i}{3}\right) \tag{12}$$

for every $i = 1, \cdots, \nu d$.

Let us consider a boundary vertex x and the associated internal angle θ of P_d. Since C_n is regular and since $\sigma < \pi/8$ in (3), we may observe the following facts. If θ is in I_1, then x needs to be two-bonded, because otherwise there would be a bond angle at x smaller than $5\pi/16$ and so not in I. Both bonds at x are then edges of P_d. If $\theta \in I_2$, then x is at most three-bonded since, otherwise, by arguing as above there would be a bound angle smaller than $3\pi/8$. Finally, for the case in which θ is in I_3 we remark that x has at most two interior bonds, still because C_n is regular. As a consequence, we get an elementary estimate on the cardinality of Γ, that is

$$\#\Gamma \leqslant d + \eta d + 2\nu d = \varepsilon d + 2\eta d + 3\nu d. \tag{13}$$

By estimates (8), (11), (12) and (13) we obtain that

$$\begin{aligned} E^{\mathrm{bnd}} &\geqslant -\varepsilon d - 2\eta d - 3\nu d + \sum_{i=1}^{\varepsilon d} E_3(\varphi_i) + 2\sum_{i=1}^{\eta d} E_3\left(\frac{\psi_i}{2}\right) + 3\sum_{i=1}^{\nu d} E_3\left(\frac{\xi_i}{3}\right) \\ &\geqslant -\varepsilon d - 2\eta d - 3\nu d + \varepsilon d E_3(\varphi) + 2\eta d E_3\left(\frac{\psi}{2}\right) + 3\nu d E_3\left(\frac{\xi}{3}\right) \\ &\geqslant -(\varepsilon{+}2\eta{+}3\nu)d + (\varepsilon{+}2\eta{+}3\nu)d E_3\left(\frac{\pi(d-2)}{(\varepsilon{+}2\eta{+}3\nu)d}\right), \end{aligned} \tag{14}$$

where we used the convexity of E_3 in I_1 in the second inequality, while the third inequality follows from (10) and again the convexity of E_3 in I_1. Therefore, we have that

$$E^{\mathrm{bnd}} \geqslant -\delta d + \delta d E_3(\alpha(\delta)), \tag{15}$$

where

$$\delta := \varepsilon + 2\eta + 3\nu \qquad \text{and} \qquad \alpha(\delta) := \frac{\pi(d-2)}{\delta d}.$$

Now, we observe that if $\delta \leqslant \delta^* := 2 - 4/d$, the assertion (9) holds true. In fact, we have

$$E^{\mathrm{bnd}} \geqslant -\delta^* d = -2d + 4, \tag{16}$$

since E_3 is always nonnegative. Thus, it remains to verify the assertion for $\delta > \delta^*$. In this case, since $\alpha(\delta) < \alpha(\delta^*) = \pi/2$, the hypothesis (4*d*) yields

$$E_3(\alpha(\delta)) \geqslant E_3\left(\frac{\pi}{2}\right) + V'_{3,-}\left(\frac{\pi}{2}\right)\left(\alpha(\delta) - \frac{\pi}{2}\right) > -\frac{2}{\pi}\left(\alpha(\delta) - \frac{\pi}{2}\right) = \frac{\delta d - 2d + 4}{\delta d}. \tag{17}$$

From the latter it easily follows that

$$-\delta d + \delta d E_3(\alpha(\delta)) \geqslant -2d + 4.$$

In view of relation (15), this completes the proof. □

An immediate corollary of the boundary-energy estimate of lemma 3.1 reads as follows.

Corollary 3.2. *Let $n \geqslant 4$ and let C_n be a connected regular configuration without flags and bridges. If C_n is nonsquare and C_n^{bulk} is square, then inequality (9) is strict.*

Proof. By following the proof of lemma 3.1 we aim at verifying that if a bond in Γ has not length 1 or a bond angle of Θ is not in $\{\pi/2, \pi, 3\pi/2\}$, then

$$E^{\mathrm{bnd}} > -2d + 4. \tag{18}$$

We begin by observing that the inequality (14) is strict if the length of a bond in Γ is not 1 or if an angle in Θ which is adjacent to an interior vertex differs from $\pi/2$, π, or $3\pi/2$, and thus in these cases relation (18) holds.

Then, we notice that $E^{\mathrm{bnd}} = -2d+4$ implies that the sum of the images through E_3 of all the bond angles in Θ is equal to $\delta d E_3(\alpha(\delta))$. Thus, if we prove that $\alpha(\delta) = \pi/2$ or, in other words, that $\delta = \delta^*$, then it would follow that all the bond angles are in $\{\pi/2, \pi, 3\pi/2\}$ and the assertion of the corollary would hold. Therefore, we are reduced to prove the following claim: $E^{\mathrm{bnd}} = -2d + 4$ implies $\delta = \delta^*$. To establish the claim we can easily show that, if $\delta \neq \delta^*$, then (18) holds. In fact, if $\delta > \delta^*$, then inequality (18) follows from relation (17), while if $\delta < \delta^*$, then the inequality in (16) is strict and this again implies the inequality (18). Hence, the claim holds and the proof is complete. □

4. Construction of candidate ground states

The aim of this section is to present by construction a family of configurations that will be later proved to be ground states in theorem 5.1. In particular, for all n we find a configuration D_n with energy

$$E(D_n) = -\beta(n),$$

where, the function β is defined by

$$\beta(n) := \lfloor 2n - 2\sqrt{n} \rfloor$$

and $\lfloor x \rfloor := \max\{z \in \mathbb{Z} \ : \ z \leqslant x\}$ denotes the lower right-continuous lower integer-part function. Let us firstly record here a remark on the function β which actually stands as an alternative (and equivalent) definition by recursion of β.

Proposition 4.1. *We have that*

$$\beta(n+1) = \beta(n) + \begin{cases} 1 & \text{if } n = m^2 \text{ or } n = m^2 + m \text{ for some } m \in \mathbb{N} \\ 2 & \text{else.} \end{cases}$$

Proof. Let us firstly discuss the case $n = m^2$. One has that $\beta(n+1) = \beta(m^2+1) = \beta(m^2) + 1$ if and only if

$$\left\lfloor 1 - 2\sqrt{m^2+1} \right\rfloor = -2m.$$

The latter is indeed equivalent to the inequalities

$$-2m \leqslant 1 - 2\sqrt{m^2+1} < -2m + 1$$

which can be easily checked.

In case n is not a square, we define $m = \lfloor\sqrt{n}\rfloor$ and let $\ell = n - m^2$ so that $1 \leqslant \ell < 2m+1$. We have that

$$\beta(n) = \beta(m^2+\ell) = 2m^2 + 2\ell^2 + \left\lfloor -2\sqrt{m^2+\ell} \right\rfloor.$$

Since $-2m-2 < -2\sqrt{m^2+\ell} < -2m$ we have that $-2m-2 \leqslant \lfloor -2\sqrt{m^2+\ell} \rfloor \leqslant -2m-1$. The assertion follows upon proving that the function $\ell \mapsto \lfloor -2\sqrt{m^2+\ell} \rfloor$ takes the values $-2m-2$ for $\ell \leqslant m$ and $-2m-1$ for $\ell \geqslant m+1$. As the latter function is monotone, it suffices to find the first integer ℓ_* such that $-2m-1 = \lfloor -2\sqrt{m^2+\ell_*} \rfloor$. Given the above considerations, such ℓ_* is the smallest integer such that

$$m + \frac{1}{2} \leqslant \sqrt{m^2+\ell}$$

which is in turn is equivalent to

$$m^2 + m + \frac{1}{4} < m^2 + \ell$$

which holds if and only if $\ell > m + 1/4$. Hence, $\ell_* = m + 1$ and the assertion follows. □

In the sequel, we will make use of the following property of the function β in order to discuss the connectedness of ground states, see theorem 5.1.

Proposition 4.2. *Let $n \geqslant 2$ and let $m < n$ be an integer. Then,*

$$\beta(n-m) + \beta(m) + 1 < \beta(n).$$

Proof. The assertion follows by computing

$$\beta(n-m) + \beta(m) + 1 \leqslant \left\lfloor 2(n - \sqrt{n-m} - \sqrt{m}) + 1 \right\rfloor \leqslant \left\lfloor 2n - 2\sqrt{n} + 1 \right\rfloor = \beta(n) + 1$$

where we have used the fact that $\sqrt{n} < \sqrt{n-m} + \sqrt{m}$. □

The main result of this section is the following proposition which provides an upper bound in the ground state energy for every $n \in \mathbb{N}$.

Proposition 4.3. *For all n there exists a configuration D_n with $E = -\beta(n)$.*

Proof. The proof consists of constructing subsets of the square lattice with exactly $\beta(n)$ bonds. This is immediate for $n \leqslant 4$. Let $n > 4$ and $m = \lfloor\sqrt{n}\rfloor$. If $n = m^2$ then the $m \times m$ square has exactly $\beta(m^2)$ bonds. If $n = m^2+\ell$ for some $1 \leqslant \ell < 2m+1$ we construct D_n by starting from the $m \times m$ square and adding progressively ℓ particles at specific sites of the square lattice. In particular, we add the first particle right above the uppermost among the leftmost particles

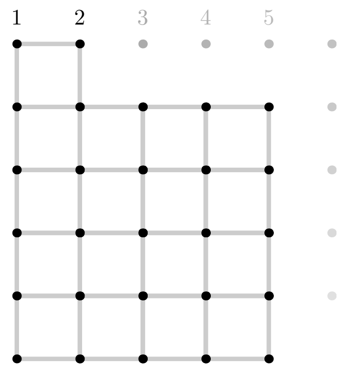

Figure 4. Construction of D_n with $E(D_n) = -\beta(n)$.

in the $m \times m$ square and then proceed clockwise by adding additional particles bonded to the previously added ones and, whenever possible, to the original $m \times m$ square, see figure 4. By means of the representation of proposition 4.1 it may be easily proved that this procedure produces a configuration with exactly $\beta(m^2+\ell)$ bonds. $\square$

5. Ground states are square

This section brings the main result of the paper, consisting of a characterization of the ground-state geometry as well as an explicit determination of the ground-state energy.

Theorem 5.1. *If C_n is a ground state, then C_n is square, connected, and*

$$E(C_n) = -\beta(n). \tag{19}$$

Proof. Thanks to proposition 2.1 we may work with regular configurations.

Let $n < 4$ and let C_n be a ground state. Since polygons with less than 4 edges are excluded in the bond graph of C_n, the maximum number of bonds is $n-1$. Thus, the assertion follows from (6) and the fact that we can easily construct square connected configurations with $n-1$ bonds. Note also that for $n = 4$ the maximum number of bonds is 4 and the unit square is the ground state. So, we now assume that the assertion holds for any ground state C_m with $m < n$ (in particular this entails that the energy of any m-particles configuration with $m < n$ is greater than or equal to $-\beta(m)$). We will prove that it holds also for C_n in some steps.

Step 1: C_n not connected. Suppose by contradiction that the ground state C_n has two or more distinct connected components. Let C_m, C_{n-m} be two subconfigurations such that no bond joins each other. By the induction assumption $E(C_n) = E(C_m) + E(C_{n-m}) \geqslant -\beta(m) - \beta(n-m)$. This implies $E(C_n) > -\beta(n)$ by using proposition 4.2, contradicting the fact that C_n is a ground state, see proposition 4.3.

Step 2: Nonsquare C_n with flags or bridges. Suppose by contradiction that the ground state C_n is nonsquare. If a bridge is there, consider the two subconfigurations C_m and C_{n-m} obtained by *removing* that bridge. If both C_m and C_{n-m} are square and C_n is not, then the bridge is not of unit length or creates an angle which is not a minimum of E_3. In particular, its contribution to the energy of C_n is strictly greater than -1. By the inductive assumption we obtain

$$E(C_n) > -\beta(m) - \beta(n-m) - 1. \tag{20}$$

If one of the two configurations C_m or C_{n-m} is not square, than $E(C_m) + E(C_{n-m}) > -\beta(m) - \beta(n-m)$ by induction. Since the bridge contribution to the energy is in general greater than or equal to -1, we still get (20). In both cases by (20) and by Proposition 4.2 we conclude that $E(C_n) > -\beta(n)$, and this contradicts the fact that C_n is a ground state. If flags are present, then there is a one-bonded particle x (the bond being a flag) and we let $C_{n-1} = C_n \setminus \{x\}$. If C_{n-1} is nonsquare, by induction $E(C_{n-1}) > -\beta(n-1)$, therefore

$$E(C_n) > -\beta(n-1) - 1 \tag{21}$$

since the energy drop in *removing* x is in modulus at most 1. Such a drop is strictly less than 1 if C_{n-1} is square, as in such case the flag under consideration is not of unit length or creates an angle which is not a minimum of E_3 (otherwise C_n would have been square itself). Then by the inductive assumption (21) still holds. In both cases, by combining (21) and $\beta(n-1)+1 \leqslant \beta(n)$ from proposition 4.1, we obtain again that $E(C_n) > -\beta(n)$, a contradiction.

Step 3. Nonsquare and connected C_n with no flags nor bridges. Owing to steps 1–2, we are left with the more relevant case of a connected ground state C_n with no flags nor bridges. Suppose by contradiction that C_n is not square. Then, either the bulk is nonsquare or we are in the assumptions of corollary 3.2. In the first case, by induction

$$E^{\text{bulk}} > -\beta(n-d).$$

In the second case, by corollary 3.2, we have

$$E^{\text{bnd}} > -2d + 4.$$

Thus, by (9) and by the fact that from the inductive hypothesis it follows that $E^{\text{bulk}} \geqslant -\beta(n-d)$, in both cases we obtain

$$E = E^{\text{bulk}} + E^{\text{bnd}} > -\left\lfloor 2(n-d) - 2\sqrt{n-d}\,\right\rfloor - 2d + 4 = -2n - \left\lfloor -2\sqrt{n-d}\,\right\rfloor + 4.$$

Since the right-hand side is integer, the strict inequality implies

$$-(\lfloor -E \rfloor + 1) \geqslant -2n + 2\sqrt{n-d} + 4. \tag{22}$$

We now prove that

$$n - d \geqslant 2(\lfloor -E \rfloor + 1) - 3n + 4, \tag{23}$$

by adapting an argument from [16, 22]. To this end, let h_j be the number of elementary j-gons in the bond graph and h be the total number of elementary polygons. We clearly have

$$\sum_{j \geqslant 1} j h_j = 2b - d,$$

and so we obtain that

$$4h \leqslant 2b - d \tag{24}$$

since all elementary polygons have at least four edges. Combining this with the Euler formula $h + n = b + 1$ we get

$$n - d \geqslant 2b - 3n + 4. \tag{25}$$

On the other hand, as C_n is not square we have from relation (6) that $E > -b$. Since b is integer, $-E < b$ implies $\lfloor -E \rfloor \leqslant b - 1$, which, together with relation (25), entails (23).

By (22) and (23) we finally obtain that

$$-(\lfloor -E \rfloor + 1) \geqslant -2n + 2\sqrt{2(\lfloor -E \rfloor + 1) - 3n + 4} + 4.$$

Since the function $x \mapsto x + 2n - 2\sqrt{-2x - 3n + 4} - 4$ is nondecreasing and vanishes at $x = -2n + 2\sqrt{n}$, the above inequality implies

$$-(\lfloor -E \rfloor + 1) \geqslant -2n + 2\sqrt{n},$$

but now the above left-hand side is integer, therefore

$$E > -(\lfloor -E \rfloor + 1) \geqslant -\left\lfloor 2n - 2\sqrt{n} \right\rfloor.$$

We have obtained $E > -\beta(n)$ which contradicts the fact that C_n is a ground state.

Step 4: Energy equality. In order to complete the induction proof we need to check that the ground state C_n enjoys (19). Since we already know that $E \leqslant -\beta(n)$ by proposition 4.3, what we are left to prove is the opposite inequality, for square connected configurations only (in the other cases C_n would fail to be a ground state by the previous steps).

As C_n is square and connected, in case it has a flag, by using induction and the fact that a flag decreases the energy at most by 1, we have that $E \geqslant -\beta(n-1) - 1$. Then, the lower bound $E \geqslant -\beta(n)$ follows by lemma 4.1. If C_n has two subconfigurations of n and $n - m$ particles connected by a bridge, by induction we find $E \geqslant -\beta(n-m) - \beta(m) - 1$. Then, the lower bound $E \geqslant -\beta(n)$ follows by applying proposition 4.2. If C_n has a single connected component, no flags and no bridges, by (7), induction, and lemma 3.1 we get that

$$E \geqslant -\beta(n-d) - 2d + 4 \geqslant -2n - \left\lfloor -2\sqrt{n-d} \right\rfloor + 4. \tag{26}$$

Next we argue as in the previous step: we observe that (25) holds and then from (6) we get $n - d \geqslant -2E - 3n + 4$, which, together with (26), yields $E \geqslant -2n + 2\sqrt{-2E-3n+4} + 4$, hence $E \geqslant -2n + 2\sqrt{n}$. But (6) holds with equality since C_n is square. In particular, E is an integer, and so the assertion $E \geqslant -\beta(n)$ follows. □

The exact quantification of the ground-state energy $E(C_n) = -\beta(n) = -\lfloor 2n - 2\sqrt{n} \rfloor$ has a number of remarkable consequences which will be illustrated in all of the remainder of the paper. It allows us not only to recover the *thermodynamic limit*

$$\lim_{n\to\infty} \frac{1}{n} E(C_n) = -2$$

in the spirit of [5, 20] but also to precisely quantify boundary effects. We shall draw from the knowledge of $E(C_n)$ a detailed geometrical description of ground states. For instance, by knowing $E(C_n)$ and using proposition 4.2 we readily check the following.

Corollary 5.2. *Ground states have no bridge.*

As far as flags are concerned, we can prove the following.

Corollary 5.3. *Let C_n be a ground state. If C_n has a flag then $n = 1, 2, 3$, $n = m^2 + 1$, or $n = m^2 + m + 1$.*

Proof. We can surely assume $n \geqslant 4$ as the other cases are easily checked. Let C_n contain a flag. Then, there is a single bonded particle x, the bond being a flag, and we consider the $(n-1)$-particle configuration $C_{n-1} := C_n \setminus \{x\}$. We compute

$$-\beta(n-1) \leqslant E(C_{n-1}) = E(C_n) + 1 = -\beta(n) + 1.$$

Owing to proposition 4.1 we conclude that $n = m^2 + 1$ or $n = m^2 + m + 1$. □

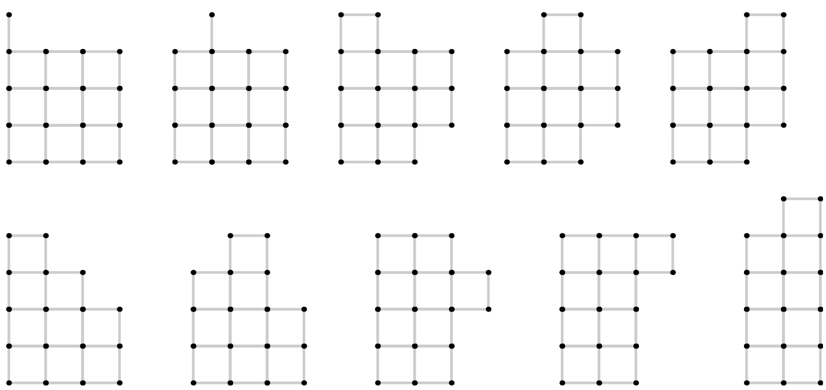

Figure 5. Nonisomorphic ground states for $n = 17$.

6. Uniqueness and defects

Ground states are generally not unique, see figure 5. Still, we have the following characterization result for some specific values of n.

Theorem 6.1. *Let C_n be a ground state for $n \geqslant 4$. If $n = m^2$ then C_n is an $m \times m$ square. If $n = m^2 + m$ then C_n is an $m \times (m+1)$ rectangle.*

Proof. Let $n = m^2$ or $n = m^2 + m$. In this case, the (boundary polygon of the) ground state C_n is necessarily convex. Indeed, if it was not convex it would present at least one reentrant corner. This would lead to the possibility of activating at least two bonds by adding an extra particle. Hence, one would have that $\beta(n+1) \geqslant \beta(n) + 2$, a possibility which is excluded by proposition 4.1.

As C_n is convex it has to coincide with an $a \times b$ rectangle. In particular, the number of bonds in C_n is $(a-1)b + (b-1)a$. By maximizing the latter over the integers under the constraint $ab = n$ we obtain the thesis. □

For all other values of n ground states are not unique. In particular, we have the following.

Corollary 6.2. *Ground states are unique for $n = 1, 2$, $n = m^2$, $n = m^2 + m$, $n = m^2 - 1$, or $n = m^2 + m - 1$ and are nonunique in all other cases.*

Proof. The assertion is obvious for $n = 1, 2$. Uniqueness for $n = m^2$ or $n = m^2 + m$ follows from theorem 6.1. For $n = m^2 - 1$ and $n = m^2 + m - 1$ the ground states correspond to an $m \times m$ square minus a two-bonded corner particle and to an $n = m^2 + m - 1$ the ground state corresponds to $m \times (m+1)$ rectangle minus a two-bonded corner particle, respectively. As such, they are unique.

Let us now come to nonuniqueness. For $n = 3$ we have exactly two ground states depending on the fact that the three particles form a π or a $\pi/2$ bond. For $n \geqslant 5$ one can consider D_n to be constructed as in the proof of proposition 4.3. If $n \neq m^2$ or $n \neq m^2 + m$ then D_n is nonconvex. It is hence possible to remove a two-bonded *corner* particle and place it in correspondence to the reentrant corner. This produces another configuration which is not isomorphic to D_n if $n \neq m^2 - 1$. This entails nonuniqueness. □

Let us close this section with another observation on the geometry of ground states.

Proposition 6.3. *Ground states are convex by rows and columns. Hence, defect-free.*

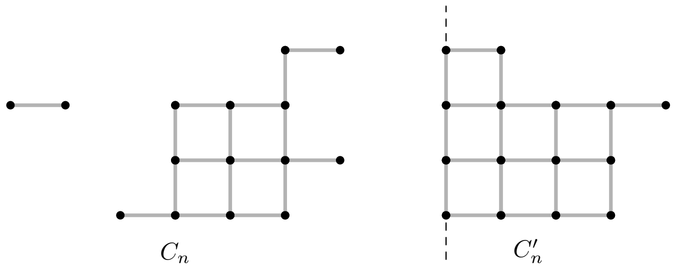

Figure 6. Construction of C'_n. One has $E(C_n) = -17$ whereas $E(C'_n) = -21$.

Proof. Given the ground state $C_n \subset \mathbb{Z}^2$, we consider the configuration

$$C'_n = \{(i, q) \in \mathbb{Z}^2 \mid \#C_n(\cdot, q) \neq 0 \text{ and } i = 1, \ldots, \#C_n(\cdot, q)\}$$

which corresponds to move particles on each row in order to make it connected and aligned, see figure 6. In case a row $C_n(\cdot, z)$ is not connected we have that $E(C'_n) < E(C_n)$ as this rearrangement activated at least one new bond. This contradicts the fact that C_n is a ground state. An analogous observation holds for columns. □

7. Ground states and discrete isoperimetric inequality

Let us consider the subproblem of minimizing E on square configurations only, that is, looking for the square configurations with maximal number of bonds. Under the *a priori* assumption that ground states are square (which is in turn something that we *prove* in theorem 5.1) energy minimization turns out to be a classical problem in discrete mathematics. In particular, by introducing the combinatorial notion of *edge perimeter* of a square configuration C_n as

$$Q(C_n) := \frac{1}{2}\,\#\left\{(x, y) \in \mathbb{Z}^2 \times \mathbb{Z}^2 \mid x \in C_n,\ y \notin C_n,\ |x - y| = 1\right\}, \tag{27}$$

we immediately check that

$$-2E(C_n) + Q(C_n) = 4n, \tag{28}$$

since each particle in $\mathbb{Z}^2$ has exactly four bonds. In particular, the square configuration that maximizes the number of bonds (that is $-E$) is the one that minimizes the edge perimeter. This corresponds to a suitable *discrete isoperimetric inequality* as argued in [10]. The reader is also referred to [1,4] for extensions to higher dimensional square lattices, and to the monograph [12] for an overview.

We shall revisit this fact in this section and sharpen the result by including an explicit quantification of the involved isoperimetric constant.

In the following, we prefer to work with suitable *geometric* notions of area and perimeter of a configuration instead of the *combinatorial* notion of edge perimeter. This change of perspective is motivated in order to highlight the geometric nature of the argument, directly relate to geometric approximations, and possibly allow extension to regular albeit nonsquare configurations.

Let C_n be a regular configuration. We denote by $F(C_n) \subset \mathbb{R}^2$ the closure of the union of the regions enclosed by the elementary cycles of C_n that have only 4 bonds (no defects), and by $G(C_n) \subset \mathbb{R}^2$ the union of all bonds in the bond graph of C_n which are not included in $F(C_n)$. Then, we may define the *area* and the *perimeter* of C_n by

$$A(C_n) := \mathcal{L}^2(F(C_n)), \qquad P(C_n) := \mathcal{H}^1(\partial F(C_n)) + 2\mathcal{H}^1(G(C_n)).$$

In the above definitions, $\mathcal{L}^2$ is the two-dimensional Lebesgue measure, $\partial F(C_n)$ is the boundary of $F(C_n)$ and $\mathcal{H}^1$ denotes the one-dimensional Hausdorff measure. Notice that $P(C_n) = d + f + 2g$ if C_n is defect-free with d boundary particles, f flags and g bridges, since acyclic bonds are counted twice. In particular, recalling corollary 5.2 and corollary 5.3, if C_n is a ground state and $n \geqslant 4$ we have that $P(C_n) = d$ if it has no flags and $P(C_n) = d+1$ otherwise (that is, if $n = m^2+1$ or $n = m^2+m+1$). Notice also that this definition of perimeter is consistent with external approximations. Indeed one can prove that

$$P(C_n) = \lim_{\varepsilon \searrow 0} \mathcal{H}^1\Big(\partial\big(\partial F(C_n) \cup G(C_n) + B_\varepsilon\big)\Big)$$

where $B_\varepsilon = \{y \in \mathbb{R}^2 \mid |y| \leqslant \varepsilon\}$. The energy of a square configuration C_n may now be rewritten in terms of a linear combination of its area and its perimeter, as expected. Namely,

$$-E(C_n) = 2A(C_n) + \frac{1}{2}P(C_n), \tag{29}$$

which corresponds to the equality case in (24) (that is, for connected defect-free square configuration without flags and bridges, in such a case d is the perimeter).

In order to deal with the isoperimetric inequality, we introduce a discrete monotone rearrangement procedure, that we call *rectangularization*, similar to the reordering of [4,10,12].

Definition 7.1. We say that a square configuration C_n is *quasirectangular*, or a *quasirectangle*, if it is connected, convex by rows and columns, and there exists a triplet (r, c, e) in

$$\mathcal{T}_n := \{(r, c, e) \in \mathbb{N}^3 \mid rc + e = n,\ 1 \leqslant e \leqslant \max\{r, c\}\}$$

such that the particles of C_n are all arranged in r rows with c particles each plus an extra connected line consisting of e particles, each bonded to one and only one particle of C_n outside of such line and such that the boundary polygon has at most one reentrant corner. We will use the notation $R_n^{r,c,e}$ for a quasirectangle with n particles organized in r rows, c columns, and in one extra line with e particles.

Examples of quasirectangles are all the configurations of section 4, see figure 4, as well as the first and the last two configurations in figure 5. Note that, since in the definition of $\mathcal{T}_n$ we excluded triples (r, c, e) with $e = 0$, the $m\times m$- square is interpreted as a quasirectangle with $(r, c, e) = (m-1, m, m)$ or $(r, c, e) = (m, m-1, m)$. This choice will simplify notation later on.

Definition 7.2. Letting C_n be a square configuration. We define its *rectangularization* $\mathcal{R}(C_n)$ as the quasirectangle resulting from rearranging the particles of C_n according to the following three steps.

(1) Rearrange C_n in C_n' by letting

$$C_n' := \{(i, q) \in \mathbb{Z}^2 \mid \#C_n(\cdot, q) \neq 0 \text{ and } i = 1, \ldots, \#C_n(\cdot, q)\}.$$

(2) Rearrange C_n' in C_n'' by letting

$$C_n'' := \{(p, j) \in \mathbb{Z}^2 \mid \#C_n(p, \cdot) \neq 0 \text{ and } j = 1, \ldots, \#C_n(p, \cdot)\}.$$

(3) Define $\mathcal{R}(C_n)$ as the configuration obtained from C_n'' by performing for $p = 2, 3, \ldots$ the following iterative procedure: if $\#C_n''(\cdot, p) < \#C_n''(\cdot, p-1)$ then move the rightmost among the uppermost particles of C_n'' to the (empty) location $(\#C_n''(\cdot, p)+1, p)$.

It is immediately realized that $\mathcal{R}(C_n)$ is a quasirectangle, hence in particular it is convex by rows and columns. The following result shows how the rectangularization interacts with energy, area, and perimeter.

Lemma 7.3. *For any connected square configuration C_n we have*

(i) $E(\mathcal{R}(C_n)) \leqslant E(C_n)$;
(ii) $P(\mathcal{R}(C_n)) \leqslant P(C_n)$;
(iii) $A(\mathcal{R}(C_n)) \geqslant A(C_n)$.

Proof. We begin by observing that, in view of the equality (29), assertion (iii) is a consequence of (i) and (ii). Thus, it suffices to prove (i) and (ii).

Assertion (i) follows from the fact that the number of bonds does not decrease in the rectangularization of C_n. In fact, first in passing from C_n to C_n'' it is clear that no bonds are lost, whereas it is possible that new bonds are activated. Finally, we observe that every time it is necessary to move a particle to pass from C_n'' to $\mathcal{R}(C_n)$, we move a one or two-bonded particle to a two-bonded particle. Thus, also in this last process the total number of bonds does not decrease.

We now establish (ii). To this end, we define $e_1 := (1, 0)$ and $e_2 := (0, 1)$ and, for $i = 1, 2$, we denote by $P_i(C_n)$ the perimeter of the part of the boundary of C_n in the direction e_i. Furthermore, we observe that the projection of the bond graph of C_n onto the e_i-axis is an interval, and we denote its length by $\Pi_i(C_n)$. From the definition of perimeter it easily follows that

$$P_1(C_n) \geqslant 2\Pi_1(C_n) \qquad \text{and} \qquad P_2(C_n) \geqslant 2\Pi_2(C_n) \tag{30}$$

and that we have two equalities in (30) if and only if C_n is also convex by rows and columns. Indeed, in the latter case the perimeter of C_n is the perimeter of the smallest closed rectangle, with edges in the directions of e_1, e_2, which contains C_n. Furthermore, by definition 7.2 we observe that

$$\Pi_1(C_n) \geqslant \Pi_1(C_n') = \Pi_1(C_n'') \qquad \text{and} \qquad \Pi_2(C_n) = \Pi_2(C_n''). \tag{31}$$

Thus, by (30) and (31) we obtain

$$P(C_n) = P_1(C_n) + P_2(C_n) \geqslant 2\Pi_1(C_n'') + 2\Pi_2(C_n'') = P_1(C_n'') + P_2(C_n'') = P(C_n'') \tag{32}$$

where we used that C_n'' is convex by rows and columns. Finally, when we need to move a two-bonded particle in passing from C_n'' to $\mathcal{R}(C_n)$ the perimeter does not change while when we need to move a flag into a two-bonded particle the perimeter strictly decreases by two. Therefore we obtain $P(C_n'') \geqslant P(\mathcal{R}(C_n))$, which together with (32) concludes the proof of assertion (ii). $\square$

A consequence of the above construction is the following.

Corollary 7.4. *Let C_n be a connected square configuration. The following assertions are equivalent:*

(a) C_n is a ground state,
(b) C_n minimizes perimeter over connected square configurations of n-particles,
(c) C_n maximizes area over connected square configurations of n-particles.

Proof. If (a) $\Leftrightarrow$ (b) holds, then (b) $\Leftrightarrow$ (c) follows immediately from equality (29). Thus, we are reduced to establish the equivalence between (a) and (b). From the proof of proposition 7.3, we see that if (b) holds, C_n is necessarily convex by rows and columns (otherwise we would get a strict inequality in (30) and then we would find $P(\mathcal{R}(C_n)) < P(C_n)$ against (b)). As a consequence, $P(C_n)$ is the perimeter of the rectangle with edges $\Pi_1(C_n)$, $\Pi_2(C_n)$, the notation being still the one of (30). Since C_n is convex by rows and columns, it is also clear that $Q(C_n) = P(C_n) + 4$. By this relation, with (28) and proposition 6.3 we see that C_n minimizes the edge perimeter (whose minimality also implies convexity by rows and columns) and we infer that C_n is a ground state. On the other hand, if (a) holds, by proposition 6.3 C_n is convex by rows and columns, then similarly we conclude that C_n is a minimizer for both Q and P. □

From the previous corollary it follows in particular that on ground states the quantities E, P, and A are invariant by $\mathcal{R}$. More precisely, we are provided with the possibility of characterizing *all* ground states for those n for which nonuniqueness occurs, see section 6. Indeed every ground state corresponds to a quasirectangle and we can list all the quasirectangular ground states. In particular, all ground states can be obtained by transforming quasirectangle ground states and thus can, at least in principle, be enumerated and described.

We are ready for the isoperimetric characterization of ground states. In the following, we let $\lceil\cdot\rceil$ denote the left-continuous upper integer-part function $\lceil x\rceil = \min\{z \in \mathbb{Z} \ : \ x \leqslant z\}$.

Theorem 7.5. *Let C_n be a connected square configuration, $n > 1$. Then,*

$$\sqrt{A(C_n)} \leqslant k_n P(C_n) \tag{33}$$

where the isoperimetric constant k_n is given by

$$k_n = \frac{\sqrt{n - \lceil 2\sqrt{n} - 1\rceil}}{2\lceil 2\sqrt{n} - 1\rceil - 2}. \tag{34}$$

Moreover, equality corresponds to ground states.

Proof.

Step 1. Let us start by checking the inequality (33). In view of lemma 7.3 it suffices to establish inequality (33) for quasirectangles. Thus, let us define k_n by

$$k_n := \max_{(r,c,e)\in\mathcal{T}_n} \frac{\sqrt{A\left(R_n^{r,c,e}\right)}}{P\left(R_n^{r,c,e}\right)} \tag{35}$$

where we recall that $R_n^{r,c,e}$ denotes the quasirectangle with n particles organized in r rows, c columns and in one extra line with $e = n - rc$ particles (definition 7.1). It is immediate to check that the area and the perimeter of a quasirectangle $R_n^{r,c,e}$ are respectively given by

$$\begin{aligned} A(R_n^{r,c,e}) &= (r-1)(c-1) + e - 1 = n - (r + c),\\ P(R_n^{r,c,e}) &= 2(r-1) + 2(c-1) + 2 = 2(r + c) - 2. \end{aligned} \tag{36}$$

Hence, (35) is equivalent to

$$k_n = \max\left\{ \frac{\sqrt{n - (r+c)}}{2(r+c) - 2} \,\middle|\, r, c \in \mathbb{N} \text{ and } n - \max\{r, c\} \leqslant rc < n \right\}.$$

As the function under maximization in the previous formula decreases with respect to $r + c$, k_n is realized at the minimum admissible value of $r + c$, i.e.,

$$k_* := \min\{r + c \mid r, c \in \mathbb{N} \text{ and } n - \max\{r, c\} \leqslant rc < n\}.$$

We claim that

$$k_* = \lceil 2\sqrt{n} - 1\rceil \tag{37}$$

To prove the claim, we first remove the constraint that restricts r and c to be integers. In fact, it is easy to verify that

$$k := \min\{r + c \mid n - \max\{r, c\} \leqslant rc < n\}$$

is equal to $2\sqrt{n} - 1$. As $k_* = \lceil k\rceil$, we obtain (37). Consequently, we can compute k_n and see that it is given by (34).

Step 2. We now show that every ground state C_n satisfies (33) with the equality. We begin by observing that if D_n is the configuration constructed in proposition 4.3, then

$$\sqrt{A(D_n)} = k_n P(D_n). \tag{38}$$

In fact, this is an easy consequence of

$$2\lfloor\sqrt{n}\rfloor = \lceil 2\sqrt{n} - 1\rceil \qquad \text{for } 1 \leqslant n - (\lfloor\sqrt{n}\rfloor)^2 \leqslant \lfloor\sqrt{n}\rfloor$$

and of

$$2\lfloor\sqrt{n} + 1\rfloor = \lceil 2\sqrt{n} - 1\rceil \qquad \text{for } \lfloor\sqrt{n}\rfloor \leqslant n - (\lfloor\sqrt{n}\rfloor)^2 \leqslant n - 1.$$

Since D_n is a ground state by proposition 4.3 and theorem 5.1, we may apply corollary 7.4 to both the ground states D_n and C_n and obtain that $P(C_n) = P(D_n)$ and $A(C_n) = A(D_n)$. Therefore, from (38) it follows that $\sqrt{A(C_n)} = k_n P(C_n)$.

Step 3. In this last step we consider a connected square configuration C_n such that

$$\sqrt{A(C_n)} = k_n P(C_n), \tag{39}$$

and we prove that C_n is a ground state. Denote again by D_n the ground state provided by proposition 4.3 and note that D_n minimizes perimeter over among square n-particles configurations by corollary 7.4. Then, we get

$$\begin{aligned} E(D_n) \leqslant E(C_n) &= -2A(C_n) - \frac{1}{2}P(C_n) = -2k_n^2 P^2(C_n) - \frac{1}{2}P(C_n) \\ &\leqslant -2k_n^2 P^2(D_n) - \frac{1}{2}P(D_n) = E(D_n), \end{aligned}$$

where we used (29), (39) and (38). This shows that $E(C_n) = E(D_n)$ and concludes the proof. □

In view of theorem 7.5 we are able deduce explicit formulas for area and perimeter of ground states. In particular, we have this further characterization of ground states.

Corollary 7.6. *Let C_n be a connected square configuration. The following assertions are equivalent:*

(a) C_n *is a ground state,*
(b) $A(C_n) = n - \lceil 2\sqrt{n} - 1\rceil$,
(c) $P(C_n) = 2\lceil 2\sqrt{n} - 1\rceil - 2$.

Proof. By corollary 7.4 ground states minimize the perimeter and maximize the area among square n-particles configurations. Moreover there are quasirectangular ground states, see proposition 4.3 Hence, the assertion follows from (36) and (37). □

Notice that the above characterizations of area and perimeter are consistent with (19) via equality (29). Indeed, by corollary 7.6 we have that C_n is a ground state if and only if

$$\begin{aligned} -E(C_n) &= 2A(C_n) + \frac{1}{2}P(C_n) = 2(n - \lceil 2\sqrt{n} - 1\rceil) + \frac{1}{2}(2\lceil 2\sqrt{n} - 1\rceil - 2) \\ &= 2n - \lceil 2\sqrt{n} - 1\rceil - 1 = \beta(n). \end{aligned}$$

8. Ground states converge to squares as $n \to \infty$

Theorem 6.1 provides a complete geometric characterization of ground states for specific values of n. For all other values, nonuniqueness occurs. Note that, even by restricting this to the class of quasirectangles, no uniqueness holds. Indeed, it suffices to consider the quasirectangles identified by the triples (9, 9, 7) and (10, 8, 8) which are both ground states but not isomorphic.

The aim of this last section is to provide some precise description of the *aspect ratio* of ground states in case of nonuniqueness. We show that ground states *approach* a square as the number of particles n gets large. We give a quantitative description of this phenomenon in the following theorem 8.1 where we state that the Hausdorff distance between a ground state C_n and the square of side $\lfloor\sqrt{n}\rfloor$ is of order $n^{1/4}$. In particular, suitably rescaled ground states converge to the square. More precisely, by letting C_n be a ground state and $G_n = C_n/\sqrt{n} := \{x/\sqrt{n} \mid x \in C_n\}$, we prove that $G_n \to [0, 1]^2$ (up to isometries) with respect to the Hausdorff topology.

In this respect, let us mention the analysis by Yeung *et al* [24] where an analogous observation was made for the triangular-lattice case. In that paper, the description of the limiting geometry and the emergence of a hexagonal macroscopic Wulff shape was investigated by Γ-convergence. See also in this context Alicandro *et al* [2]. Our approach is quite different as we concentrate on minimizers instead (rather than on energies) and provide a sharp quantitative estimate in terms of Hausdorff topology *for all* n. We have the following.

Theorem 8.1. *The ground state C_n approaches the square S_n of side $\lfloor\sqrt{n}\rfloor$ as n gets large. Precisely, we have that*

$$d(C_n, S_n') \leqslant \frac{1}{2}n^{1/4} + 1$$

where d is the Hausdorff distance and $S_n' = S_n + a$ for some $a \in \mathbb{R}^2$.

Proof. Let C_n be a ground state and $\ell_1, \ell_2 \in \mathbb{N}$ be the number of particles of the minimal $\ell_1 \times \ell_2$ rectangular configuration including C_n. Recall that ground states are convex by rows and columns and so we have two equalities in (30), thus $\ell_1 = \Pi_1(C_n) + 1$, $\ell_2 = \Pi_2(C_n) + 1$. Assume with no loss of generality that $\ell_1 \geqslant \ell_2$. Then, by corollary 7.6 (c) we have that

$$P(C_n) = 2\lceil 2\sqrt{n}-1\rceil - 2 = 2((\ell_2-1) + (\ell_1-1))$$

so that, in particular, $\ell_1 + \ell_2 = k_* + 1$, where k_* is given by relation (37). We shall hence consider the maximization problem

$$\max\{\ell_1 - \ell_2 \;:\; \ell_1, \ell_2 \in \mathbb{N},\ n \leqslant \ell_1\ell_2,\ \ell_1 + \ell_2 = k_* + 1\}$$

which can be solved analytically. We can compute the optimal pair $(\ell_1^*, k_*+1-\ell_1^*)$ which corresponds to

$$\ell_1^* = \left\lfloor \frac{(k_*+1) + \sqrt{(k_*+1)^2-4n}}{2} \right\rfloor = \left\lfloor \frac{\lceil 2\sqrt{n}\rceil + \sqrt{(\lceil 2\sqrt{n}\rceil)^2-4n}}{2} \right\rfloor.$$

In particular, the maximal value of $\ell_1 - \ell_2$ reads

$$\begin{aligned}
\ell_1 - \ell_2 = 2\ell_1^* - k_* - 1 &= 2\left\lfloor \frac{\lceil 2\sqrt{n}\rceil + \sqrt{(\lceil 2\sqrt{n}\rceil)^2-4n}}{2} \right\rfloor - \lceil 2\sqrt{n}-1\rceil - 1 \\
&\leqslant 2\left\lfloor \frac{\sqrt{(\lceil 2\sqrt{n}\rceil)^2-4n}}{2} \right\rfloor \leqslant \sqrt{(\lceil 2\sqrt{n}\rceil)^2-4n} \leqslant \sqrt{(2\sqrt{n}+1)^2-4n} \\
&= \sqrt{4\sqrt{n}+1} \leqslant 2n^{1/4} + 1.
\end{aligned}$$

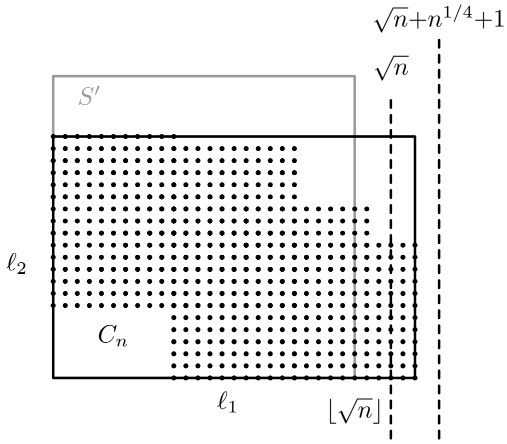

Figure 7. Construction for the proof of theorem 8.1. Note that the depicted configuration C_n is chosen for illustrative purposes only. In particular, it is not a ground state.

As we have that $\ell_2 = \lceil 2\sqrt{n}\rceil - \ell_1$, from $\ell_2 \leqslant \ell_1 \leqslant \ell_2 + 2n^{1/4} + 1$ we deduce that

$$\frac{1}{2}\lceil 2\sqrt{n}\rceil \leqslant \ell_1 \leqslant \frac{1}{2}\lceil 2\sqrt{n}\rceil + n^{1/4} + \frac{1}{2}.$$

By using the elementary inequalities $x \leqslant \lceil x\rceil \leqslant x + 1$ we obtain

$$\sqrt{n} \leqslant \ell_1 \leqslant \sqrt{n} + n^{1/4} + 1.$$

Correspondingly, we also have that $\sqrt{n} - n^{1/4} - 1 \leqslant \ell_2 \leqslant \sqrt{n}$. In particular, by referring to the notation of figure 7, one can check that $d(C_n, S') \leqslant n^{1/4} + 2$ so that the assertion follows by translating S' (to the right). □

For the sake of completeness and of comparison with [24], we conclude this section by restating the above aspect-ratio result in terms of weak∗-convergence of empirical measures. Indeed, assume $C_n = \{x_1, \ldots, x_n\}$ to be a ground state and let μ_n be the probability measure in $\mathbb{R}^2$ given by

$$\mu_n = \frac{1}{n}\sum_i \delta_{x_i/\sqrt{n}}.$$

Then, theorem 8.1 entails in particular that, up to isometries, $\mu_n \to \mu$ in the weak∗ sense where μ is the Lebesgue measure restricted to the square $[0, 1]^2$. The latter observation corresponds to the square-lattice version of the former [24, theorem 1.2]. In particular, given two ground states $C_n, G_n \subset \mathbb{Z}^2$ we have that

$$d(C_n, G_n') \leqslant n^{1/4} + 3$$

where $G_n' = G_n + a$ for some $a \in \mathbb{Z}^2$. As the diameter of a ground state is controlled by $\sqrt{2n} + \mathrm{O}(n^{1/4})$, we readily conclude that

$$\#(C_n \triangle G_n') \leqslant \sqrt{2}n^{3/4} + \mathrm{O}(n^{1/2}).$$

That is, two n-particles ground states differ at most by $\mathrm{O}(n^{3/4})$ particles.

This same conclusion has recently been obtained by Schmidt [19] in the frame of the so-called Heitmann–Radin *sticky* potentials. These correspond to choose $v = 0$ in (2) and $E_3 = 0$ entailing finite crystallization on the triangular lattice [13]. Also in this case, ground states deviate at most by $\mathrm{O}(n^{3/4})$ particles from the ideal (hexagonal) Wulff shape configuration.

Acknowledgment

Ulisse Stefanelli and Paolo Piovano acknowledge the partial support of the FP7-IDEAS-ERC-StG grant no 200947 *BioSMA* and CNR-JSPS grant *VarEvol*.

References

[1] Ahlswede R and Bezrukov S L 1995 Edge isoperimetric theorems for integer point arrays *Appl. Math. Lett.* **8** 75–80
[2] Alicandro R, Braides A and Cicalese M 2008 Continuum limits of discrete thin films with superlinear growth densities *Calc. Var. Partial Diff. Eqns* **33** 267–97
[3] Blanc X and Le Bris C 2002 Periodicity of the infinite-volume ground state of a one-dimensional quantum model *Nonlinear Anal.* **48** 791–803
[4] Bollobas B and Leader I 1991 Edge-isoperimetric inequalities in the grid *Combinatorica* **11** 299–314
[5] E W and Li D 2009 On the crystallization of 2D hexagonal lattices *Commun. Math. Phys.* **286** 1099–140
[6] Flatley L and Theil F 2012 Face-centered cubic crystallization of atomistic configurations, submitted
[7] Flatley L, Taylor M, Tarasov A and Theil F 2013 Packing twelve spherical caps to maximize tangencies *J. Comput. Appl. Math.* **254** 220–5
[8] Gardner C S and Radin C 1979 The infinite-volume ground state of the Lennard-Jones potential *J. Stat. Phys.* **20** 719–24
[9] Hamrick G C and Radin C 1979 The symmetry of ground states under perturbation *J. Stat. Phys.* **21** 601–7
[10] Harary F and Harborth H 1976 Extremal animals *J. Combin. Inform. Syst. Sci.* **1** 1–8
[11] Harborth H 1974 Solution to problem 664A *Elem. Math.* **29** 14–5
[12] Harper L H 2004 *Global Methods for Combinatorial Isoperimetric Problems* (*Cambridge Studies in Advanced Mathematics* vol 90) (Cambridge: Cambridge University Press)
[13] Heitmann R and Radin C 1980 Ground states for sticky disks *J. Stat. Phys.* **22** 281–7
[14] Le Bris C and Lions P-L 2005 From atoms to crystals: a mathematical journey *Bull. Amer. Math. Soc.* **42** 291–363
[15] Mainini E and Stefanelli U 2014 Crystallization in carbon nanostructures *Commun. Math. Phys.* at press
[16] Radin C 1981 The ground state for soft disks *J. Stat. Phys.* **26** 365–73
[17] Radin C 1986 Crystals and quasicrystals: a continuum model *Commun. Math. Phys.* **105** 385–90
[18] Radin C and Schulmann L S 1983 Periodicity of classical ground states *Phys. Rev. Lett.* **51** 621–2
[19] Schmidt B 2013 Ground states of the 2D sticky disc model: fine properties and $N^{3/4}$ law for the deviation from the asymptotic Wulff shape *J. Stat. Phys.* **153** 727–38
[20] Theil F 2006 A proof of crystallization in two dimensions *Commun. Math. Phys.* **262** 209–36
[21] Ventevogel W J and Nijboer B R A 1979 On the configuration of systems of interacting particle with minimum potential energy per particle *Physica* A **98** 274–88
[22] Wagner H J 1983 Crystallinity in two dimensions: a note on a paper of C Radin *J. Stat. Phys.* **33** 523–6
[23] Yedder A B, Blanc X and Le Bris C 2003 A numerical investigation of the two-dimensional crystal problem www.ljll.math.upmc.fr/publications/2003/R03003.html
[24] Yeung Y A, Friesecke G and Schmidt B 2012 Minimizing atomic configurations of short range pair potentials in two dimensions: crystallization in the Wulff shape *Calc. Var. Partial Diff. Eqns* **44** 81–100