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No crystallization to honeycomb or Kagomé in free space

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Abstract

It is intuitive that if an infinite system of particles that interact through an isotropic potential has a crystalline ground state at zero chemical potential, it is of high symmetry. Here, we present an argument why a honeycomb or a Kagomé structure cannot be the ground state at zero chemical potential, for a large class of potentials in $\mathbb{R}^2$.

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1. Introduction

The phenomenon of crystallization has attracted both computational and theoretical interest over the years. On the theoretical side, the question of existence and characterization of crystalline ground states for systems of particles interacting through two-body potentials has proven to be a difficult one. Some of the earlier results in this direction, e.g. [1], were limited to 1D systems. More recently, there has been some good progress for 2D and 3D systems: in [2], it was proved that a class of isotropic interaction potentials resembling the Lennard–Jones potential have the triangular lattice as their (grand canonical) ground state at zero chemical potential in 2D. Moreover, in [3], a class of potentials were studied (those with a non-negative Fourier transform that vanishes above a wave number), and it was found that, at certain densities, the triangular lattice (in 2D) and the bcc lattice (in 3D) are the ground states of these potentials. In [4], the existence (without characterization) of periodic ground states for a large class of many-body interactions was established.

A question relevant to the characterization of crystalline ground states for infinite systems of interacting particles is which periodic configurations may be candidates for ground states of a given isotropic potential and which may not. Intuition suggests that if the minimum energy state over all densities (ground state at zero chemical potential) is crystalline at all, it is one of high symmetry, e.g. a triangular or square lattice in 2D and a bcc, fcc or hcp lattice in 3D. Numerical studies support this intuition. For example, a large system of particles in $\mathbb{R}^2$ interacting through a Lennard–Jones potential will equilibrate at $T = 0$ in a configuration

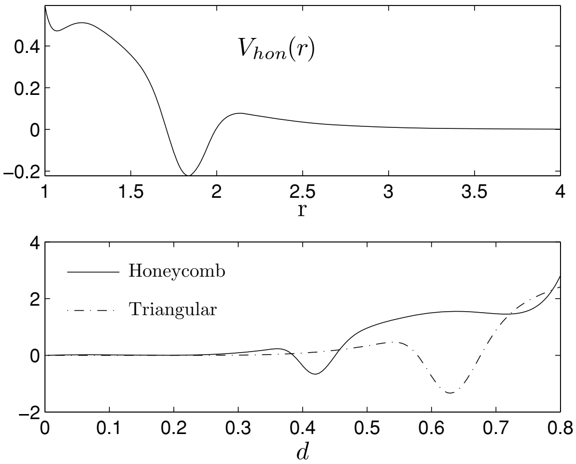

Figure 1. Top: $V_{\mathrm{hon}}(r)$. Bottom: epp for triangular lattice and honeycomb structure for V_{hon} as functions of density.

that is, to a good approximation, a piece of triangular lattice. In this example, the particle system 'chooses its own density' in the process of minimizing its total energy and assembles into the highest symmetry 2D lattice. In [5], a potential is given that assembles particles into an approximate honeycomb structure (as T decreases to 0) for a specific particle density. The potential $V_{\mathrm{hon}}(r)$ is plotted in figure 1 (top graph). The bottom figure shows the graphs of the energy per particle (epp) for triangular and honeycomb structures, as functions of particle density. Although there are density ranges where the epp of the honeycomb structure is lower than that of the triangular lattice, the minimum epp of the triangular lattice (over all densities) is lower than the minimum epp of the honeycomb. Hence, the ground state at zero chemical potential (no particle density constraint) cannot be a honeycomb structure, because there are triangular lattices with smaller epp.

In this paper we prove that, for a large class of isotropic potentials, the honeycomb and Kagomé structures cannot be ground states at zero chemical potential for an infinite system of particles. Our results hold with minimum technical assumptions on the inter-particle potential: the potential can be soft or hard core and need only decay fast enough at infinity. The results are essentially geometrical in nature. In each case, we prove that the energy per particle (epp) of the periodic configuration of interest at density d is equal to a convex combination of the epp of two triangular lattices with densities d_1 and d_2 (d_1 and d_2 are proportional to d but different from it). Hence, for the configuration of interest at density d, there exists another crystalline state (with density d_1 or d_2) that has lower epp. Under appropriate conditions, this implies that the said periodic configuration cannot be the ground state at zero chemical potential for a wide class of potential forms (note, however, that the said configuration can well be the ground state for a range of values of d). Although a general understanding of the applicability of this method is lacking at this moment, it could be applied to other low-symmetry 2D/3D structures.

This paper is organized as follows. In section 2, we review the decomposition of a general periodic structure in terms of an underlying Bravais lattice, and the corresponding decomposition of its epp. Using this decomposition, in section 3 we express the epp of the honeycomb and the Kagomé structures, as convex combinations of the epp of triangular lattices. The consequences of the results of section 3 for crystallization in free space are discussed in section 4. Section 5 concludes the paper.

2. Decomposition of periodic structures and their epp in terms of simple lattices

Consider a (finite or infinite) system of identical classical particles in $\mathbb{R}^2$ with two-body interactions. The potential energy of a configuration of particles in positions $\{\mathbf{r}_i\}$ is given by

$$U_{\text{int}} = \frac{1}{2}\sum_{i\neq j} V(\mathbf{r}_i - \mathbf{r}_j),$$

where $V(\mathbf{r})$ is the potential of the pairwise interactions. Note that self-energy contributions $V(\mathbf{0})$ are excluded from the total potential energy. We make the following assumptions about V:

(1) V is isotropic, i.e. $V(\mathbf{r}) = V(r)$. This is the most common situation when the interacting particles have no shape/internal structure.
(2) $V(r) = +\infty$ for $0 \leqslant r \leqslant r_c$ and finite for $r > r_c$ ($r_c \geqslant 0$ is the radius of the hard core). When $r_c = 0$, $V(0)$ may be finite, but this is unimportant since we exclude self-energy contributions from the total potential energy.
(3) The function $r|V(r)|$ is absolutely integrable at infinity. This assumption is necessary for the absolute convergence of the series that define the epp of the infinite periodic configurations of particles we consider. The absolute convergence of these series is also necessary for their re-arrangements throughout the paper.

Consider a 2D Bravais lattice $\Lambda \doteq \{n\mathbf{e}_1 + m\mathbf{e}_2, n, m \in \mathbb{Z}\}$, where $\mathbf{e}_1$ and $\mathbf{e}_2$ are two linearly independent vectors in $\mathbb{R}^2$. Let D be a bounded simply connected domain of $\mathbb{R}^2$ and $\#D$ the number of lattice sites inside D. Let

$$U(D) \doteq \frac{1}{2}\sum_{\mathbf{r}_i\neq\mathbf{r}_j\in D} V(\mathbf{r}_i - \mathbf{r}_j)$$

denote the total interaction energy of the particles occupying lattice sites inside D. The limit of $U(D)/\#D$ as D approaches infinity in the sense of Van Hove defines the epp U_0 of the lattice. The existence of this limit is implied by well-established results in the literature on the existence of the thermodynamic limit for the specific free energy [6]. As is well known and intuitively clear,

$$U_0 = \frac{1}{2}\sum_{\substack{n,m=-\infty \\ (n,m)\neq(0,0)}}^{+\infty} V(n\mathbf{e}_1 + m\mathbf{e}_2). \tag{1}$$

In the following, we consider discrete periodic structures in $\mathbb{R}^2$ that are not simple (Bravais) lattices. Formally, such structures can be expressed as $\cup_{a=1}^{q}(\Lambda + \mathbf{b}_a) = \cup_{a=1}^{q}\{n\mathbf{e}_1 + m\mathbf{e}_2 + \mathbf{b}_a, n, m \in \mathbb{Z}\}$, for some vectors $\mathbf{b}_a, a = 1, \ldots, q$. The vectors $\mathbf{b}_a, a = 1, \ldots, q$ are called the basis of the periodic structure and must be contained in the parallelepiped ('cell') defined by the lattice vectors $\mathbf{e}_1$ and $\mathbf{e}_2$. We say that 'the periodic structure is decomposed in terms of the lattice Λ'. Such a decomposition of a periodic structure is by no means unique. Also, even simple lattices can be decomposed in terms of other lattices. As examples, we mention the following:

(1) The triangular lattice of lattice constant $l = 1$, $\left\{n\hat{\mathbf{x}} + m\left(\frac{1}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}}{2}\hat{\mathbf{y}}\right)\right\}$, can be decomposed in terms of an orthogonal lattice, with $\mathbf{e}_1 = \hat{\mathbf{x}}, \mathbf{e}_2 = \sqrt{3}\hat{\mathbf{y}}$ and basis $\left\{\mathbf{b}_1 = \mathbf{0}, \mathbf{b}_2 = \frac{1}{2}\left(\hat{\mathbf{x}} + \sqrt{3}\hat{\mathbf{y}}\right)\right\}$.
(2) A honeycomb structure ($l = 1$), whose hexagonal cells are stacked parallel to the y-direction, can be decomposed in terms of an orthogonal lattice, with $\mathbf{e}_1 = 3\hat{\mathbf{x}}, \mathbf{e}_2 = \sqrt{3}\hat{\mathbf{y}}$ and basis $\left\{\mathbf{b}_1 = \hat{\mathbf{x}}, \mathbf{b}_2 = -\hat{\mathbf{x}}, \mathbf{b}_3 = \frac{1}{2}(\hat{\mathbf{x}} + \sqrt{3}\hat{\mathbf{y}}), \mathbf{b}_4 = -\frac{1}{2}\left(\hat{\mathbf{x}} + \sqrt{3}\hat{\mathbf{y}}\right)\right\}$.

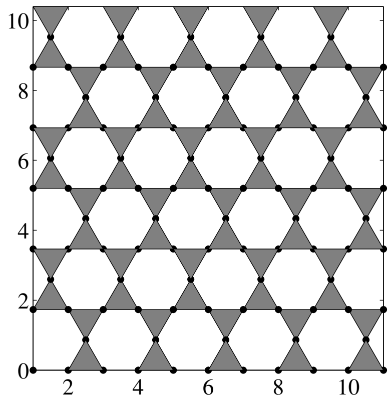

Figure 2. A Kagomé structure of $l = 1$.

(3) The Kagomé structure ($l = 1$) of figure 2 can be decomposed in terms of a triangular lattice, with $\mathbf{e}_1 = 2\hat{\mathbf{x}}$, $\mathbf{e}_2 = \hat{\mathbf{x}} + \sqrt{3}\hat{\mathbf{y}}$ and basis $\left\{\mathbf{b}_1 = \mathbf{0}, \mathbf{b}_2 = \hat{\mathbf{x}}, \mathbf{b}_3 = \frac{1}{2}(\hat{\mathbf{x}} + \sqrt{3}\hat{\mathbf{y}})\right\}$.

The epp can also be defined for general periodic structures with the following intuitive result generalizing (1):

$$U_0 \doteq \frac{1}{q} \sum_{a,b=1}^{q} \frac{1}{2} \sum_{n,m=-\infty}^{+\infty} V(n\mathbf{e}_1 + m\mathbf{e}_2 + \mathbf{b}_a - \mathbf{b}_b). \tag{2}$$

In the next section, this 'decomposition' of the epp of a periodic structure in terms of the underlying lattice will be used to relate the epp of the honeycomb and Kagomé structures to the epp of triangular lattices.

We close this section with a simple example that will be useful in the following. We derive the epp for a triangular lattice of $l = 1$, using its decomposition in terms of an orthogonal lattice given in example 1. From now on, $V(\mathbf{0})$ is implicitly omitted from all the infinite sums where it would occur. We have from the definition (2),

$$\begin{aligned} U_0 &= \frac{1}{2} \sum_{a,b=1}^{2} \frac{1}{2} \sum_{n,m=-\infty}^{+\infty} V(n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}} + \mathbf{b}_a - \mathbf{b}_b) \\ &= \frac{1}{4} \sum_{n,m=-\infty}^{+\infty} V(n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}}) + \frac{1}{4} \sum_{n,m=-\infty}^{+\infty} V(n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}}) \\ &\quad + \frac{1}{4} \sum_{n,m=-\infty}^{+\infty} V\left(n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}} + \frac{1}{2}(\hat{\mathbf{x}} + \sqrt{3}\hat{\mathbf{y}})\right) \\ &\quad + \frac{1}{4} \sum_{n,m=-\infty}^{+\infty} V\left(n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}} - \frac{1}{2}(\hat{\mathbf{x}} + \sqrt{3}\hat{\mathbf{y}})\right). \end{aligned}$$

The first two sums have terms of the form $V(n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}} + \mathbf{b}_a - \mathbf{b}_a)$, $a = 1, 2$ and are equal. The last two have terms of the form $V(n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}} \pm (\mathbf{b}_a - \mathbf{b}_b))$ with $a = 1$ and $b = 2$. These two sums are equal as well. The easiest way to see this is to rename the dummy (summation) indices n and m in the last sum as $-n$ and $-m$. The summation limits do not change because each sum is in $\mathbb{Z}$. Then, use the property $V(-\mathbf{r}) = V(\mathbf{r})$ to turn the last sum into the third sum:

$$\sum_{n,m=-\infty}^{+\infty} V\left(n\hat{\mathbf{x}}+\sqrt{3}m\hat{\mathbf{y}}-\frac{1}{2}(\hat{\mathbf{x}}+\sqrt{3}\hat{\mathbf{y}})\right)$$
$$=\sum_{n,m=-\infty}^{+\infty} V\left(-n\hat{\mathbf{x}}-\sqrt{3}m\hat{\mathbf{y}}-\frac{1}{2}(\hat{\mathbf{x}}+\sqrt{3}\hat{\mathbf{y}})\right)$$
$$=\sum_{n,m=-\infty}^{+\infty} V\left(n\hat{\mathbf{x}}+\sqrt{3}m\hat{\mathbf{y}}+\frac{1}{2}(\hat{\mathbf{x}}+\sqrt{3}\hat{\mathbf{y}})\right).$$

Hence,

$$U_0=\frac{1}{2}\sum_{n,m=-\infty}^{+\infty} V(n\hat{\mathbf{x}}+\sqrt{3}m\hat{\mathbf{y}})+\frac{1}{2}\sum_{n,m=-\infty}^{+\infty} V\left(n\hat{\mathbf{x}}+\sqrt{3}m\hat{\mathbf{y}}+\frac{1}{2}(\hat{\mathbf{x}}+\sqrt{3}\hat{\mathbf{y}})\right).$$

For a periodic structure of constant l/density d, we denote its epp by $U_0(\text{structure name}, l)$/ $U_0(\text{structure name}, d)$. In this notation, the equation above can be stated as

$$U_0(\text{tri}, l=1)=\frac{1}{2}\sum_{n,m=-\infty}^{+\infty} V(n\hat{\mathbf{x}}+\sqrt{3}m\hat{\mathbf{y}})+\frac{1}{2}\sum_{n,m=-\infty}^{+\infty} V\left(n\hat{\mathbf{x}}+\sqrt{3}m\hat{\mathbf{y}}+\frac{1}{2}(\hat{\mathbf{x}}+\sqrt{3}\hat{\mathbf{y}})\right).$$

By letting $\hat{\mathbf{x}}\to\hat{\mathbf{y}}$ and $\hat{\mathbf{y}}\to\hat{\mathbf{x}}$ and multiplying all lengths by $\sqrt{3}$ in this equation, we obtain the epp for a triangular lattice of lattice constant $\sqrt{3}$ rotated by $\pi/2$ with respect to that considered so far. This will be useful in the following, so we state the equation here (note that we have renamed the dummy indices, $m\to n$, $n\to m$ and shifted $n\to n+1$ in the second sum):

$$U_0(\text{tri}, l=\sqrt{3})=\frac{1}{2}\sum_{n,m=-\infty}^{+\infty} V(3n\hat{\mathbf{x}}+\sqrt{3}m\hat{\mathbf{y}})$$
$$+\frac{1}{2}\sum_{n,m=-\infty}^{+\infty} V\left(3n\hat{\mathbf{x}}+\sqrt{3}m\hat{\mathbf{y}}+\frac{1}{2}(3\hat{\mathbf{x}}+\sqrt{3}\hat{\mathbf{y}})\right).$$

3. epp of the honeycomb and Kagomé structures in terms of epp of triangular lattices

In this section, we express the epp of the honeycomb and Kagomé structures in terms of epp of triangular lattices using (2). We state the following theorem.

Theorem 1. *If the potential V satisfies the assumptions 1–3,*

$$U_0(\text{hon}, d)=\frac{1}{2}U_0\left(\text{tri}, \frac{3d}{2}\right)+\frac{1}{2}U_0\left(\text{tri}, \frac{d}{2}\right). \tag{3}$$

$$U_0(\text{Kag}, d)=\frac{2}{3}U_0\left(\text{tri}, \frac{4d}{3}\right)+\frac{1}{3}U_0\left(\text{tri}, \frac{d}{3}\right). \tag{4}$$

Proof. Given the density–lattice constant relation for the triangular, honeycomb and Kagomé lattices, $d_{\text{tri}}(l)=2/\sqrt{3}l^2$, $d_{\text{hc}}(l)=4/3\sqrt{3}l^2$ and $d_{\text{kg}}(l)=\sqrt{3}/2l^2$, equations (3) and (4) can be restated as

$$U_0(\text{hon}, l)=\tfrac{1}{2}U_0(\text{tri}, l)+\tfrac{1}{2}U_0(\text{tri}, \sqrt{3}l). \tag{5}$$

$$U_0(\text{Kag}, l)=\tfrac{2}{3}U_0(\text{tri}, l)+\tfrac{1}{3}U_0(\text{tri}, 2l). \tag{6}$$

It suffices to prove these statements for $l = 1$, as the general result follows by rescaling. Using the decomposition of the honeycomb structure in terms of an orthogonal lattice given in the last section, we have

$$U_0(\text{hon}, l = 1) = \frac{1}{4}\sum_{a,b=1}^{4}\frac{1}{2}\sum_{n,m=-\infty}^{+\infty} V(3n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}} + \mathbf{b}_a - \mathbf{b}_b),$$

where

$$\mathbf{b}_1 = \hat{\mathbf{x}}, \qquad \mathbf{b}_2 = -\hat{\mathbf{x}}, \qquad \mathbf{b}_3 = \frac{1}{2}(\hat{\mathbf{x}} + \sqrt{3}\hat{\mathbf{y}}) \qquad \text{and} \qquad \mathbf{b}_4 = -\frac{1}{2}(\hat{\mathbf{x}} + \sqrt{3}\hat{\mathbf{y}}).$$

Out of the 16 sums in $U_0(\text{hon}, 1)$, four have terms of the form $V(3n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}} + \mathbf{b}_a - \mathbf{b}_a) = V(3n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}})$, and hence are equal. The remaining 12 sums come in pairs such that one has terms of the form $V(3n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}} + \mathbf{b}_a - \mathbf{b}_b)$, and the other $V(3n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}} + \mathbf{b}_b - \mathbf{b}_a)$, $a \neq b$. Again, the two sums are equal. Then,

$$\begin{aligned}
U_0(\text{hon}, l = 1) = {} & \frac{1}{4}\sum_{n,m=-\infty}^{+\infty} V(3n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}}) && (A1)\\
& + \frac{1}{4}\sum_{n,m=-\infty}^{+\infty} V(3n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}}) && (A2)\\
& + \frac{1}{4}\sum_{n,m=-\infty}^{+\infty} V(3n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}} + 2\hat{\mathbf{x}}) && (B)\\
& + \frac{1}{4}\sum_{n,m=-\infty}^{+\infty} V\left(3n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}} + \frac{1}{2}\hat{\mathbf{x}} - \frac{\sqrt{3}}{2}\hat{\mathbf{y}}\right) && (C)\\
& + \frac{1}{4}\sum_{n,m=-\infty}^{+\infty} V\left(3n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}} + \frac{3}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}}{2}\hat{\mathbf{y}}\right) && (D)\\
& + \frac{1}{4}\sum_{n,m=-\infty}^{+\infty} V\left(3n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}} - \frac{3}{2}\hat{\mathbf{x}} - \frac{\sqrt{3}}{2}\hat{\mathbf{y}}\right) && (E)\\
& + \frac{1}{4}\sum_{n,m=-\infty}^{+\infty} V\left(3n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}} - \frac{1}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}}{2}\hat{\mathbf{y}}\right) && (F)\\
& + \frac{1}{4}\sum_{n,m=-\infty}^{+\infty} V(3n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}} + \hat{\mathbf{x}} + \sqrt{3}\hat{\mathbf{y}}). && (G)
\end{aligned}$$

For sums over $n \in \mathbb{Z}$ and $m \in \mathbb{Z}$, finite shifts in the summation indices, e.g. $n \to n \pm 1$, $m \to m \pm 1$ preserve the sums. Note that such operations will not take place in sums $(A1)$ and $(A2)$ where $V(\mathbf{0})$ is excluded. Hence, we can write as follows:

$$(C, m \to m+1) = \frac{1}{4}\sum_{n,m=-\infty}^{+\infty} V\left(3n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}} + \frac{1}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}}{2}\hat{\mathbf{y}}\right),$$

$$(E, n \to n+1, m \to m+1) = \frac{1}{4}\sum_{n,m=-\infty}^{+\infty} V\left(3n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}} + \frac{3}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}}{2}\hat{\mathbf{y}}\right),$$

$$(F, n \to n+1) = \frac{1}{4}\sum_{n,m=-\infty}^{+\infty} V\left(3n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}} + \frac{5}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}}{2}\hat{\mathbf{y}}\right),$$

$$(G, m \to m-1) = \frac{1}{4} \sum_{n,m=-\infty}^{+\infty} V(3n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}} + \hat{\mathbf{x}}).$$

Next, we arrange the sums as follows:

$$\begin{aligned}
U_0(\text{hon}, l=1) = {} & \frac{1}{4} \sum_{n,m=-\infty}^{+\infty} V(3n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}}) && (A1)\\
& + \frac{1}{4} \sum_{n,m=-\infty}^{+\infty} V(3n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}} + \hat{\mathbf{x}}) && (G)\\
& + \frac{1}{4} \sum_{n,m=-\infty}^{+\infty} V(3n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}} + 2\hat{\mathbf{x}}) && (B)\\
& + \frac{1}{4} \sum_{n,m=-\infty}^{+\infty} V\left(3n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}} + \frac{1}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}}{2}\hat{\mathbf{y}}\right) && (C)\\
& + \frac{1}{4} \sum_{n,m=-\infty}^{+\infty} V\left(3n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}} + \frac{3}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}}{2}\hat{\mathbf{y}}\right) && (D)\\
& + \frac{1}{4} \sum_{n,m=-\infty}^{+\infty} V\left(3n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}} + \frac{5}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}}{2}\hat{\mathbf{y}}\right) && (F)\\
& + \frac{1}{4} \sum_{n,m=-\infty}^{+\infty} V(3n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}}) && (A2)\\
& + \frac{1}{4} \sum_{n,m=-\infty}^{+\infty} V\left(3n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}} + \frac{3}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}}{2}\hat{\mathbf{y}}\right). && (E)
\end{aligned}$$

Now, note that

$$(A1) + (G) + (B) = \frac{1}{4} \sum_{n,m=-\infty}^{+\infty} V(n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}})$$

$$(C) + (D) + (F) = \frac{1}{4} \sum_{n,m=-\infty}^{+\infty} V\left(n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}} + \frac{1}{2}(\hat{\mathbf{x}} + \sqrt{3}\hat{\mathbf{y}})\right),$$

hence,

$$\begin{aligned}
U_0(\text{hon}, l=1) \\
&= \frac{1}{4} \sum_{n,m=-\infty}^{+\infty} V(n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}}) + \frac{1}{4} \sum_{n,m=-\infty}^{+\infty} V\left(n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}} + \frac{1}{2}(\hat{\mathbf{x}} + \sqrt{3}\hat{\mathbf{y}})\right)\\
&\quad + \frac{1}{4} \sum_{n,m=-\infty}^{+\infty} V(3n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}}) + \frac{1}{4} \sum_{n,m=-\infty}^{+\infty} V\left(3n\hat{\mathbf{x}} + \sqrt{3}m\hat{\mathbf{y}} + \frac{3}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}}{2}\hat{\mathbf{y}}\right)\\
&= \frac{1}{2} U_0(\text{tri}, l=1) + \frac{1}{2} U_0(\text{tri}, l=\sqrt{3}),
\end{aligned}$$

where the expressions for the epp of triangular lattices of constants 1 and $\sqrt{3}$ given at the end of the last section were used.

For the Kagomé structure, using its decomposition in terms of a triangular lattice given in example 3 of the last section, we have

$$
\begin{aligned}
U_0(\text{Kag}, l=1) &= \frac{1}{2}\sum_{n,m=-\infty}^{+\infty} V(2n\hat{\mathbf{x}} + m(\hat{\mathbf{x}} + \sqrt{3}\hat{\mathbf{y}})) \\
&\quad + \frac{1}{3}\sum_{n,m=-\infty}^{+\infty} V(2n\hat{\mathbf{x}} + m(\hat{\mathbf{x}} + \sqrt{3}\hat{\mathbf{y}}) + \hat{\mathbf{x}}) \\
&\quad + \frac{1}{3}\sum_{n,m=-\infty}^{+\infty} V\left(2n\hat{\mathbf{x}} + m(\hat{\mathbf{x}} + \sqrt{3}\hat{\mathbf{y}}) + \frac{1}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}}{2}\hat{\mathbf{y}}\right) \\
&\quad + \frac{1}{3}\sum_{n,m=-\infty}^{+\infty} V\left(2n\hat{\mathbf{x}} + m(\hat{\mathbf{x}} + \sqrt{3}\hat{\mathbf{y}}) + \frac{3}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}}{2}\hat{\mathbf{y}}\right) \\
&= \frac{1}{6}\sum_{n,m=-\infty}^{+\infty} V(2n\hat{\mathbf{x}} + m(\hat{\mathbf{x}} + \sqrt{3}\hat{\mathbf{y}})) \\
&\quad + \frac{1}{3}\left(\sum_{n,m=-\infty}^{+\infty} V(2n\hat{\mathbf{x}} + m(\hat{\mathbf{x}} + \sqrt{3}\hat{\mathbf{y}}))\right. \\
&\quad \left. + \sum_{n,m=-\infty}^{+\infty} V(2n\hat{\mathbf{x}} + m(\hat{\mathbf{x}} + \sqrt{3}\hat{\mathbf{y}}) + \hat{\mathbf{x}})\right) \\
&\quad + \frac{1}{3}\left(\sum_{n,m=-\infty}^{+\infty} V\left(2n\hat{\mathbf{x}} + m(\hat{\mathbf{x}} + \sqrt{3}\hat{\mathbf{y}}) + \frac{1}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}}{2}\hat{\mathbf{y}}\right)\right. \\
&\quad \left. + \sum_{n,m=-\infty}^{+\infty} V\left(2n\hat{\mathbf{x}} + m(\hat{\mathbf{x}} + \sqrt{3}\hat{\mathbf{y}}) + \frac{3}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}}{2}\hat{\mathbf{y}}\right)\right) \\
&= \frac{1}{3}U_0(\text{tri}, l=2) \\
&\quad + \frac{1}{3}\sum_{n,m=-\infty}^{+\infty} V(n\hat{\mathbf{x}} + m(\hat{\mathbf{x}} + \sqrt{3}\hat{\mathbf{y}})) \\
&\quad + \frac{1}{3}\sum_{n,m=-\infty}^{+\infty} V\left(n\hat{\mathbf{x}} + m(\hat{\mathbf{x}} + \sqrt{3}\hat{\mathbf{y}}) + \frac{1}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}}{2}\hat{\mathbf{y}}\right) \\
&= \frac{1}{3}U_0(\text{tri}, l=2) + \frac{2}{3}U_0(\text{tri}, l=1).
\end{aligned}
$$

□

4. No crystallization to honeycomb or Kagomé structures in free space

In this section, we work out the implications of (3) and (4) for crystallization in free space, i.e without imposing any restriction on the particle density. Let us begin with (3). Whenever $U_0\left(\text{tri}, \frac{3d}{2}\right) \neq U_0\left(\text{tri}, \frac{d}{2}\right)$, it implies that $U_0(\text{hon}, d) > \min\left\{U_0\left(\text{tri}, \frac{3d}{2}\right), U_0\left(\text{tri}, \frac{d}{2}\right)\right\}$. Hence, a honeycomb structure of density d has greater epp than a triangular lattice of density $\frac{d}{2}$ or $\frac{3d}{2}$, and so it cannot be the global ground state. If $U_0\left(\text{tri}, \frac{3d}{2}\right) \neq U_0\left(\text{tri}, \frac{d}{2}\right)$ holds for all $d > 0$, no honeycomb structure (of any density) can be the global ground state. What happens if there are density values d_i^* such that $U_0\left(\text{tri}, \frac{3d_i^*}{2}\right) = U_0\left(\text{tri}, \frac{d_i^*}{2}\right)$? As long as

$\min_d U_0(\text{tri}, d) < U_0\big(\text{tri}, \frac{d_i^*}{2}\big) = U_0\big(\text{tri}, \frac{3d_i^*}{2}\big)$ for all d_i^*, $\min_d U_0(\text{tri}, d) < \min_d U_0(\text{hon}, d)$ and again, no honeycomb structure can be the ground state at zero chemical potential. So, as long as $U_0(\text{tri}, d)$ does not attain its global minimum at two density values $\frac{d^*}{2}$ or $\frac{3d^*}{2}$ for some $d^* > 0$, no honeycomb structure of any density can be the ground state at zero chemical potential for the corresponding potential.

As a simple example, we consider potentials of the form

$$V(r) = \frac{c_q}{r^q} - \frac{c_p}{r^p}$$

in $\mathbb{R}^m$, with $c_q, c_p > 0$ and $q > p > m + 1$. These potentials satisfy our basic assumptions. It is easy to see that

$$U_0(\text{tri}, l) = \frac{c_q g_q}{l^q} - \frac{c_p g_p}{l^p}$$

with

$$g_s \doteq \frac{1}{2} \sum_{\substack{n,m=-\infty \\ (n,m)\neq(0,0).}}^{+\infty} \frac{1}{\left\| n\hat{\mathbf{x}} + m\left(\frac{1}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}}{2}\hat{\mathbf{y}}\right)\right\|^s}, \qquad s = q, p.$$

In terms of density, we have that

$$U_0(\text{tri}, d) = \frac{3^{q/4} c_q g_q}{2^{q/2}} d^{q/2} - \frac{3^{p/4} c_p g_p}{2^{p/2}} d^{p/2}.$$

From the form of $U_0(\text{tri}, d)$ it is seen that it has a unique minimum at

$$d = \frac{2}{\sqrt{3}} \left(\frac{p c_p g_p}{q c_q g_q}\right)^{\frac{2}{q-p}},$$

so a honeycomb structure cannot be the ground state for these potentials.

An identical analysis can be performed for the case of the Kagomé structure and (4). We state these results together:

Theorem 2. *Let the potential V satisfy assumptions 1–3.*

(1) A necessary condition for a honeycomb structure to be the ground state at zero chemical potential for an infinite system of particles interacting through V in $\mathbb{R}^2$ is that $U_0(\text{tri}, d)$ attains its global minimum at two density values $\frac{d^*}{2}$ or $\frac{3d^*}{2}$ for some $d^* > 0$, i.e. there exists $d^* > 0$ such that $\min_d U_0(\text{tri}, d) = U_0\big(\text{tri}, \frac{d^*}{2}\big) = U_0\big(\text{tri}, \frac{3d^*}{2}\big)$.

(2) A necessary condition for a Kagomé structure to be the ground state at zero chemical potential for an infinite system of particles interacting through V in $\mathbb{R}^2$ is that $U_0(\text{tri}, d)$ attains its global minimum at two density values $\frac{d^*}{3}$ or $\frac{4d^*}{3}$ for some $d^* > 0$, i.e. there exists $d^* > 0$ such that $\min_d U_0(\text{tri}, d) = U_0\big(\text{tri}, \frac{d^*}{3}\big) = U_0\big(\text{tri}, \frac{4d^*}{3}\big)$.

The essence of our argument that the honeycomb and Kagomé structures cannot be formed in free space is the fact that conditions 1 and 2 are non-generic for realistic potentials. In the case that a potential satisfies, say, condition 1, there are two alternatives: first, the honeycomb structure is not a ground state because there is another structure with lower epp, say a square lattice; second, the honeycomb structure is a ground state, but it is not unique. Indeed, in view of condition 1 and (3), one concludes that there are two triangular lattices at densities $\frac{d^*}{2}$ and $\frac{3d^*}{2}$ (d^* is the density of the honeycomb) that are also ground states. Similarly, if a Kagomé structure of density d^* is a ground state for a potential, there are two triangular lattices at densities $\frac{d^*}{3}$ and $\frac{4d^*}{3}$ that are also ground states. Also, it is not clear which of the ground state structures will form in free space as the particle system is cooled down to $T = 0$. Hence, even if the conditions exist for the honeycomb or the Kagomé structure to be the global energy minimum, it is never unique and is probably not assembled from all initial conditions of the particle system.

5. Summary

Using the decompositions of the honeycomb and Kagomé structures in terms of simple lattices, we were able to express their epp as convex combinations of epp of triangular lattices and derive necessary conditions for them to be ground states at zero chemical potential. These conditions should be violated for a large class of potentials. We also argued that, even when these conditions are met, the structures under consideration are non-unique ground states and hence their formation through freezing is uncertain.

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