Jammed systems of oriented needles always percolate on square lattices

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Random sequential adsorption (RSA) is a standard method of modeling adsorption of large molecules at the liquid-solid interface. Several studies have recently conjectured that in the RSA of rectangular needles, or \( k \)-mers, on a square lattice the percolation is impossible if the needles are sufficiently long (\( k \) of order of several thousand). We refute these claims and present a strict proof that in any jammed configuration of nonoverlapping, fixed-length, horizontal or vertical needles on a square lattice, all clusters are percolating clusters.

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I. INTRODUCTION

Adsorption of large molecules like polymers, biomolecules or nanotubes at the liquid-solid interface is an important part of various natural and technological processes, including those found in industrial bioreactors [1], water purification [2], or production of conducting nanocomposites [3]. In many cases the adsorption phenomenon is essentially an irreversible and localized process in which the adsorbed molecules eventually form a monolayer on the target surface [4]. It is therefore quite common to investigate such phenomena using the random sequential adsorption (RSA) model. The main idea behind it is simple [4–6]: starting with an empty substrate, one tries to put on it a sequence of some geometric objects, e.g. disks or rectangles, each at a random position. An attempt is successful if the new object does not overlap with the ones already deposited on the surface, otherwise a new attempt is made at a different, randomly chosen location. Once the object is attached to the surface, it stays there motionless forever, reducing a chance for the subsequent molecules to be adsorbed in its neighborhood. The dynamics gradually slows down and finally no unoccupied room remains on the substrate that could accommodate the next object—the process stops, the system has reached the so-called jamming limit (a discussion of various aspects of jamming configurations can be found in the review [7]).

Numerous extensions of the basic RSA model have been studied so far, including imperfect substrates [8, 9], various object shapes (e.g., disks [4], spheres [10], spherocylinders [11], infinitely thin needles [12], squares [13, 14], ellipses [15], and rectangles [8, 9, 15–19]), polydispersity [20–22], shape flexibility [23, 24], post-adsorption dynamics (e.g., desorption [25] and diffusion [26]), and partial [27] or full object overlapping [28]. In each RSA process, basic or extended one, as the molecules are being deposited onto the surface, they may touch each other and form larger clusters of connected (or “neighboring”) objects, and if such a cluster spans the opposite sides of the system, we have to do with a percolating cluster.

Consequently, there are two basic quantities characterizing RSA processes. The first one is the jamming threshold \( 0 < c_j < 1 \) defined as the ratio of the surface area covered by the adsorbed objects (\( A_{ad} \)) to the total surface area (\( A \)) in the jammed state. The second one is the percolation threshold \( c_p \), a quantity similar to the jamming threshold in that it is also defined as \( A_{ad}/A \), except that \( A_{ad} \) must be now determined at the moment when the adsorbed molecules start to form a percolating cluster [29]. While \( c_j \) characterizes any RSA process, \( c_p \) is well defined only for some of them. For example, in models where nonoverlapping objects, e.g. circles, are randomly deposited on a continuous substrate, e.g. a larger square, no object can actually touch another one and a percolating cluster cannot be formed. However, the information whether (or under which conditions) an RSA process leads to percolation or not is a fundamental characteristic of this process.

In 2000 Vandewalle et al. [17] advanced a hypothesis that in the RSA of needle-like rectangles (also known as \( k \)-mers) on a square lattice the ratio \( c_p/c_j \) is constant for all needle sizes. If correct, this hypothesis would indicate existence of a deep relation between jamming and percolation. However, more elaborate studies refuted this claim. Instead, as will be discussed in detail in Section II, several researchers came to the conclusion that for sufficiently long needles the system does not percolate. However, this striking conjecture is based on extrapolation of numerical results obtained for relatively short needles and no physical mechanism responsible for such a behavior is known.

Thus, analysis of the above-mentioned reports raises the question of percolation breakdown. Does percolation really break down for very long needles or is it an artifact brought about by using an incorrect fitting function to the numerical data? There seems to be two ways towards the solution. The first one is to carry out a direct numerical examination of percolation for extremely long needles. However, this would require using so huge amounts of computer resources (memory and computational time) that such simulations have not been undertaken yet [8]. The other option is to prove or disprove the conjecture mathematically. The second option is more
attractive, especially since exact arguments in percolation theory are relatively rare. Here we present such a strict proof that any cluster in a jammed configuration of fixed-length needles on a square lattice is a percolating cluster. Consequently, the RSA of fixed-length needles always percolates on a square lattice.

II. CONTRIBUTIONS TO THE HYPOTHESIS OF THE PERCOLATION BREAKDOWN

In their study of RSA of needles on a square lattice, Kondrat et al. [18] noticed a peculiar dependence of the ratio of the percolation threshold to the jamming threshold \( c_p/c_j \) on the needle length \( k \),

\[
c_p/c_j \approx a + b \log_{10} k,
\]

with \( a = 0.50 \) and \( b = 0.13 \). Since \( c_p/c_j \) cannot be greater than 1, it was clear that this relation must break for needles of length larger than some characteristic length \( k_* \), which in this case can be estimated as \( 10^{(1-a)/b} \approx 7000 \). Equation (1) was put forward as a phenomenological formula based on numerical results for needles of rather moderate length \( k \leq 45 \), which raised the question: is \( k_* \) a real physical parameter and if so, what happens to \( c_p/c_j \) as \( k \) approaches and then exceeds \( k_* \)?

This problem was tackled by Tarasevich et al. [19], who studied the RSA of partially ordered needles. In the isotropic case they confirmed relation (1) for much longer needles \( (k \leq 512) \) and also obtained more accurate estimates of parameters \( a = 0.513(6) \) and \( b = 0.119(3) \), which implies \( k_* = 12\,400(3700) \). As the logarithmic formula was verified for really long needles, the problem of what happens close to and beyond \( k_* \) became more interesting. Assuming that (1) is valid up to \( k_* \), they formulated the hypothesis that for \( k \geq k_* \) the system does not percolate and the ratio \( c_p/c_j \) simply becomes undefined, which would solve the paradox.

This rather surprising conclusion was confirmed in a study of random sequential adsorption of needles in imperfect systems [8]. Two extensions of the original model were considered: either the needles have some imperfect (nonconducting) segments (a so called K model) or the underlying lattice nodes. Two needles are connected directly if they share a part of their sides of length \( k \geq 1 \) l.u. so that for \( k = 1 \) the problem reduces to the classical site percolation. Of course, we consider only systems large enough to accommodate at least one needle. Moreover, since the theorem is trivial for \( k = 1 \), henceforth we assume that \( k > 1 \) and one can divide the needles into horizontal and vertical ones.

Below we present two different methods of proving this theorem, as each of them can potentially be used in more general cases e.g., for lattices other than the square one [30] or in higher space dimensions [31].

A. Method I

For convenience, we start from proving the following Lemma: Every cluster at a jammed configuration extends to one of two consecutive edges of the system. If one labels the system edges using the geographical notation \((N, E, S, W)\) and \((W, N)\), the lemma states that any cluster at jamming must touch at least one edge in each of the four pairs: \((N, E)\), \((E, S)\), \((S, W)\), and \((W, N)\).

We will prove the Lemma a contrario—let us assume that there exists a jammed configuration of fixed-length

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FIG. 1. An exemplary cluster with the topmost cell in each lattice column marked with a dot. Orientation (horizontal or vertical) of the needles occupying these cells can be used to classify the corresponding lattice columns as H or V. If the rightmost column is of type V and the rightmost needle (“EV-needle”) does not touch the edge of the system, there is a room, marked with a hatched pattern, for another needle.

nonoverlapping needles with a cluster that does not touch any of two consecutive system edges, say N and E.

Since the system is a square lattice of size $L \times L$ ($L \geq k$), it can be regarded as a set of $L$ columns, each made of $L$ elementary lattice cells. For each column we can identify the set of all its cells that belong to the cluster. If this set is nonempty, we can use the topmost cell from this set to classify the column as follows: if the column’s topmost cell belongs to a horizontal needle, the column is said to be of type H, otherwise the cell belongs to a vertical needle and the column is said to be of type V. This is illustrated in Fig. 1.

Consider now the rightmost column containing the sites from our cluster. We will label it $c_{HE}$ because it is cluster’s easternmost column and it is of type H. To see the reason for the latter property, suppose this column is of type V. In such a case it would contain at least one vertical needle (marked as an EV-needle in Fig. 1). Since we assumed that the cluster does not touch system’s edge E, there exists a column to the right of the EV-needle and it contains at least $k$ consecutive empty sites, see Fig. 1. This, however, contradicts the assumption that the system is jammed.

There are now two possibilities: either all columns with the sites from the cluster are of the same type H or at least one of these columns is of type V. We will consider each of these cases separately.

1. **Case A: all columns are of type H**

Let $r_N$ denote the topmost row containing the cluster (see Figure 2). As all columns are assumed to be of type H, this row must contain at least one horizontal needle, which we will call “NH-needle”. As no cell above the topmost row can belong to the cluster and since we have assumed that the cluster does not touch system edge N, all cells neighboring the NH-needle from above are empty and can accommodate another needle. As this contradicts the assumption that the system is jammed, the proof of case A is completed.

2. **Case B: columns of mixed types, H and V**

Consider now the case where at least one column is of type V. Let $c_{VE}$ denote the rightmost column of type V. Cluster’s topmost cell in this column belongs to a vertical needle, which we call the EV-needle (see Fig. 3). Its bottom cell defines a reference row, which we denote as $r_{VS}$. We also define $r_{HN}$ as the topmost row containing a horizontal needle to the right of the EV-needle. The remaining part of the proof depends on the relation between $r_{VS}$ and $r_{HN}$.

a. **Case B1: $r_{VS} > r_{HN}$**. In this case all cells of the cluster that are to the right of column $c_{VE}$ lie below
row \( r_{VS} \). This means that the cells located directly to the right of the EV-needle are unoccupied and can accommodate another needle, see Fig. 4. This, however, contradicts the assumption that the system is jammed.

b. Case B2: \( r_{VS} \leq r_{HN} \). Let “NH-needle” denote the rightmost horizontal needle located at row \( r_{HN} \). Each cell occupied by this needle lies to the right of the EV-needle (see Fig. 5). Directly above the NH-needle there are neither vertical needles (all columns to the right of column \( c_{VE} \) are of type H), nor horizontal ones (otherwise the NH-needle would not be the topmost one).

Thus, the cells neighboring the NH-needle from above are empty and can accommodate another needle. However, this contradicts the assumption that the system is jammed. This completes the proof of the Lemma.

The final step is to show that the Lemma implies the Theorem. Let us assume that the there is a jammed configuration of needles and a cluster in it. There are two cases: either this cluster extends to all four edges of the system or not. In the former case the cluster is trivially a percolating cluster. In the latter one it does not touch at least one system edge, say, N. However, the Lemma ensures that in this case it must extend to the two edges adjacent to N, that is, to E and W, and hence must be a percolating cluster.

**B. Method II**

Suppose that it is possible to fill a finite square lattice of size \( L \times L \), \( L \geq k \), with nonoverlapping horizontal or vertical needles of size \( 1 \times k \) in such a way that the system is jammed and a cluster of connected needles exists such that it does not touch the system borders. We will show that this assumption leads to a contradiction.

Let us define the hull of a cluster as the minimal simple polygon encompassing it, see Fig. 6. This polygon is made of horizontal and vertical line segments of integer length. It divides the plane into the space occupied by the cluster together with, perhaps, some holes between the needles forming it, and the remaining space.

By construction, any elementary square bordering the hull from inside must be occupied by some needle, whereas none of the squares bordering the hull from the outside can be occupied by a needle, see Fig. 6. Thus, the length of any side of the hull is an integer less than \( k \), otherwise one could add a needle on the squares bordering this side from the outside, which contradicts the assumption that the system is jammed.

Each horizontal line segment of the hull is followed by a vertical one and so forth by turns, so that the number of its vertices, \( N \), is even and the angles at its vertices are either \( \pi/2 \) or \( 3\pi/2 \). Let \( q_+ \) and \( q_- \) denote the number of \( \pi/2 \) and \( 3\pi/2 \) angles, respectively. Since the sum of internal angles of an \( N \)-sided polygon is \( (N-2)\pi \), these quantities satisfy \( q_+ + q_- = N \) and \( q_+ \pi/2 + q_- (3\pi/2) = \)
(N − 2)\pi. Consequently,

\[ q_+ = N/2 + 2, \quad q_- = N/2 - 2. \]

Let us assign to each vertex \( i \) of the hull an integer \( a_i \in \{-1, 1\} \) such that \( a_i = 1 \) if the internal angle at \( i \) is \( \pi/2 \) and \( a_i = -1 \) if this angle is \( 3\pi/2 \). The idea is that as we walk along the hull in a clockwise direction, we keep track of our current orientation by adding 1 whenever we make a right turn and subtracting 1 for the left turn. From (4) we have

\[ \sum_{i=0}^{N-1} a_i = q_+ - q_- = 4, \]

that is, whenever we return to the starting point, we must have made 4 more right turns than the left ones. Let \( s_i = (a_i + a_{i+1})/2 \) (throughout the paper we apply to the indices the modular arithmetic with modulus \( N \)). By construction, \( s_i \) are also integers, \( s_i \in \{-1, 0, 1\} \), which measure the effect of making two consecutive turns. They satisfy

\[ \sum_{i=0}^{N-1} s_i = \sum_{i=0}^{N-1} a_i = 4. \]

In the sequence \( s_0, s_1, \ldots, s_{N−1} \) there are thus at least two indices \( j < k \) such that \( s_j = s_k = 1 \) and \( s_l = 0 \) for all \( j < l < k \). Therefore there exist two vertices, \( j \) and \( k \), such that \( a_j = a_{j+1} = 1 \) and \( a_k = a_{k+1} = 1 \), separated, perhaps, by an alternating sequence of the form \( -1, 1, \ldots, -1 \). Geometrically this corresponds to a “zigzag” ended by two “caps”, see Fig. 7a.

Each cap uniquely determines the orientation (horizontal or vertical) of the needles that occupy it. This is because the length of the cap side connecting two consecutive right angles is smaller than \( k \), and so any needle touching it from inside must be perpendicular to it (cf. Fig. 7b). Moreover, if the zig-zag segment exists between the two caps, each of the caps enforces the direction of the needles touching the zig-zag segment to be parallel to the needles filling in that cap. However, the orientations of the two consecutive caps are orthogonal to each other. This leads to a contradiction: the needles touching the zig-zag cannot be all both horizontal and vertical (Fig. 7c).

If, however, no zig-zag part exists, then \( k = j + 1 \) and \( a_j = a_{j+1} = a_{j+2} = 1 \), that is, the cap has two consecutive, orthogonal sides of size smaller than \( k \). Such a region cannot be filled by needles of length \( k \), which again contradicts our assumptions. Thus, either the hull of the cluster touches one of the edges of a finite system, in which case at least one side touching the edge is of length \( \geq k \), or the system is not jammed.

Is it possible that a cluster at a jamming state touches only one of the system’s edges? If such a cluster existed, it could be used to construct a cluster made of needles of size \( 1 \times k \), whose hull is a polygon with all sides of lengths \( < k \), see Fig. 8. However, we have just proven that such a cluster does not exist. The construction is defined as follows. One takes the original cluster as well as its mirror reflection and joins them together with two needles sticking out with \( k - 1 \) of their \( k \) elementary segments. Each side of the resulting cluster would be smaller than \( k \). Moreover, the two extra needles cannot overlap, for the original cluster must touch the system edge at least \( k \geq 2 \) different lattice cells (corresponding to a longer side of one of its needles). If this construction generates one or more holes inside the new hull, one can fill them up with additional needles in an arbitrary way.

Thus any cluster at a jamming state must touch at least two edges of the system. If a cluster touches exactly two consecutive edges of the system, one could use a construction similar to that described in the previous
paragraph twice, once in the horizontal and once in the vertical direction, to construct a cluster made of needles $1 \times k$, whose hull is a polygon with all sides of lengths $< k$. However, such a cluster does not exist. Consequently, any cluster at a jamming state connects two opposite sides of the system, horizontally or vertically, and therefore is a percolating cluster.

IV. CONCLUSIONS AND OUTLOOK

We have proved that all jammed configurations of nonoverlapping needles of size $1 \times k$ ($k$-mers) on a square lattice are percolating ones. This disproves the recent conjecture [8, 9, 19] that in the random sequential adsorption of such needles on a square lattice the percolation does not occur if the needles are longer than some threshold value $k_\ast$, estimated to be of order of several thousand. While this result ensures that the percolation to jamming ratio ($c_p/c_\ast$) is well defined for all needle lengths, it does not bring us much closer to the understanding of how this ratio varies with $k$ for $k \gtrsim 500$. Perhaps the only way of obtaining this information is through numerical simulations, but this would require either to employ supercomputers or to devise much more efficient algorithms tailored to this specific problem.

Our theorem has some implications for other RSA problems. For example, in the case of the RSA on an imperfect lattice [8], we can use it to conclude that any cluster formed in the jammed, nonpercolating state must have at least two “nonconducting” lattice cells at its perimeter, both adjacent to the sides of the hull whose length is $\geq k$. This helps to understand why even a tiny lattice impurity can preclude percolation in systems with very long needles: one impurity per cluster hull side can be enough to stop its growth.

Another interesting point is whether our arguments can be extended to other lattices, e.g. the triangular or cubic ones.

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