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AN INTERACTING PARTICLE MODEL OF ADSORPTION

Abstract. We propose a general lattice model for the study of the dynamics of adsorption (desorption) processes on surfaces. Basically, the model involves an interacting particle system on a two-dimensional (square or triangular) lattice, where the rates of birth (adsorption of a particle onto the lattice) are constant, and the rates of death (desorption) depend only on the neighborhood pattern, i.e., the configuration of occupied sites surrounding the particle. Essentially, the stability of an adsorbed particle depends on its coordination number; a particle of maximum allowed coordination is least likely to desorb.

A set of Monte-Carlo simulations of this model has been conducted wherein we study the coverage of the surface as a function of time as well as its derivative (coverage current). We also propose and analyze estimates of two different quantities related to the clustering effect: the conditional entropy of the distribution of occupied sites in different patterns and an index of complexity of clusters which, essentially, is the ε-entropy of the cluster's border.

Using the general theory of interacting particle systems, we prove analytical results about the behavior of the coverage with respect to time, as well as the asymptotic properties of the model.

1. PRESENTATION OF THE MODEL

1.1. Introduction. In the past fifteen years, a large amount of theoretical, experimental and computer simulation work has been devoted to the field of adsorption (desorption) of particles on surfaces. For example see papers [19], [1], [10], which give a good idea of the breadth of this area. This body of work provided us with a motivation for developing a theory that departs from the tradition of van Kampen [21] and uses instead the theory of interacting particle systems (as presented, e.g., by Liggett [17]).

Our aim is to provide a comprehensive mathematical framework for this type of surface process and to show, by means of rigorous analysis, as well as by statistical studies of Monte-Carlo simulations, that the proposed model includes many of the features expected to be associated with adsorption (desorption) phenomena.

The first quantity of physical interest one can try to observe for this type of physical processes is the evolution of the coverage with respect to time. In experimental practice it is usually obtained indirectly by the study of its variations using such tools as chemiluminescence, quartz crystal microbalance [15], or direct measurement of induced electrical currents [6]. However, it should be emphasized that the observed current (for instance in potential step experiments) cannot always be interpreted directly as the derivative of the coverage with respect to time because of the time dependence of charging the double layer capacitance. Moreover, the coverage at a given time is, by its very nature, a discrete random variable. Thus the derivative can be considered only for its average. In order to avoid any confusion, we will use a special term: "the coverage current" to denote the derivative of the mean coverage with respect to time.

A particular feature of the observed deposition phenomena is what is customarily referred to as the clustering effect, and our model is expected to mimic it. Various hypotheses have been proposed to explain this clustering effect. The particles are believed by some (see [6]) to move on the surface itself, performing some sort of random walk which helps in bringing them together. Others (see [8], [9]) argue that the clusters are growing from a starting point, the nucleus, by a sort of a diffusion process and many models have been proposed to describe the growth of these clusters (cf., e.g., [6], [3]). The last among these references proposes a very general model taking into account the adsorption-desorption process as well as the growth of clusters.

In a recent paper, [22], we developed a simple dynamic model of adsorption-desorption for a lattice gas. This model used two Poisson processes, the rates of which, interpreted as rates λ and μ of adsorption and desorption ("births and deaths") of particles on the surface, depended only on the number of particles already adsorbed. In the case of a large number of independent sites, it was proved in [22] that the coverage follows approximately a normal law with mean

$$\frac{\lambda}{\lambda+\mu}(1-\exp[-t(\lambda+\mu)]).$$

In this case the coverage current should be expected to decay in an exponential way. However, it has been shown experimentally for different types of adsorption that it decreases actually much less rapidly than it should, were the sites independent (cf., e.g., [15]). In the second part of this paper we show what types of behavior of the coverage current to expect when interactions are included.

The model we present here, although based on the same idea of a birth and death process, is more general in the sense that the desorption dynamics of a particle at one site is allowed to depend on the state of its neighborhood. Moreover, we study not only the coverage but the global evolution of the configuration of occupied and empty sites on the surface. Although the model does not explicitly include a random walk of particles already adsorbed on the surface (which is plausible from the physical view-point), it is able to mimic the clustering effect observed in more complicated models. This can be explained as due to the adjustment of the rates of death: if the duration of life of an isolated particle is much shorter than for a surrounded one, then fewer isolated particles are likely to remain on the surface. It should also be noted that our general model does not satisfy the reversibility (i.e., detailed balance) condition (see [17], Section II.5, and [21], Chapter 5, where this condition is defined in terms of transfer matrices). As a matter of fact, in the class of spin systems with finite-range interactions only the stochastic Ising models are reversible (cf. Theorem 2.13 of [17]) and we certainly wanted to go beyond this category of particle systems. Furthermore, the assumptions imposed on our model do guarantee its ergodicity (i.e., the existence of unique equilibrium distribution) anyway (cf. Section 3.1), and this is what the detailed balance condition often is used for in the physical literature (cf. [2] or [21] for the classical transfer matrix approach).

In the first part of this paper, we present the model informally using heuristic arguments to justify the choices that were made. In the second part, we propose four parameters which we mean to describe the most important properties of our model. The first two of these parameters are the coverage and an estimate of its derivative with respect to time, which corresponds to that part of the observed current due to coverage effects. The third parameter is a measure of the clustering effect: it is the conditional entropy of the distribution of occupied sites relative to the neighborhood patterns. The last one measures the complexity of the clusters: it is an estimate of the intricacy of the clusters border. A series of Monte-Carlo experiments was conducted wherein we studied the evolution of these four parameters with respect to time. The outcomes of these experiments are presented in Section 2.2.

In Section 3, we present some results of the mathematical theory of interacting particle systems (cf. [17]). Most important is the theorem of comparison from which we derive upper and lower bounds for the evolution of the coverage with respect to time (Proposition 3.2.3). We derive also further results showing the asymptotic properties of the model.

1.2. Geometry of the lattice. We assume that during deposition onto a solid surface, the adsorbed particles tend to arrange themselves according to a pattern characterized by a regular lattice. The nature of this lattice is dictated by the geometry of the underlying crystal [13] or adsorbate-adsorbate interactions [20], or both.

The lattice sites of adsorption are taken to be the vertices of a regular planar lattice, either square or triangular. Indeed, these are the two lattices most widely discussed in the literature (see [19], [20]). Thus, our assumption is that each site has exactly four nearest neighbors in the first case and six in the second. As each site may be occupied or empty, the number of possible configurations assumed by the set of nearest neighbors of a given site is 2^4 or 2^6. For reasons of isotropy and symmetry, those numbers reduce to 6 in the case of the square lattice (Fig. 1a) and to 13 for the triangular lattice (Fig. 1b). From now on those configurations will be referred to as "neighborhood patterns".

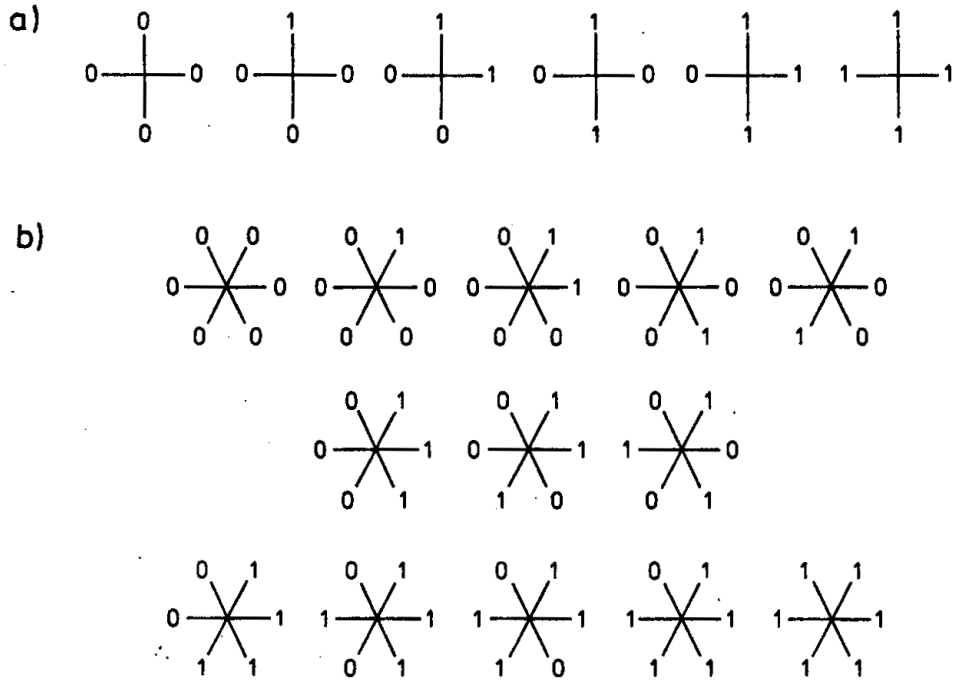

Fig. 1. *Neighborhood patterns.* Each site on the lattice may be occupied (1) or empty (0). The number of possible configurations of the nearest neighbor is *a priori* 2^4 for the square lattice, and 2^6 for the triangular lattice. However, the number of essentially different (up to rotations and symmetries) neighborhood patterns is only six for the square lattice and thirteen for the triangular lattice

In principle, the lattices may be infinite. For a finite lattice, in order to retain the property of each site to have the same number of neighbors, we consider finite parallelograms the parallel sides of which are identified, so as to form a topological torus. This procedure is classical in the study of lattice systems, and the result is usually called "periodic boundary lattice" (cf., e.g., [16], Chapter III). See Section 2.2 for more details on this.

1.3. Hypotheses. Let S be the set of all sites. With each of them we associate 0 if it is empty, and 1 if it is occupied. Then the general configuration at time t, denoted by η_t, is an element of $\{0, 1\}^S$.

We assume that η_t is a Markov process and evolves according to the following rules:

(1.3.1) The conditional probability of adsorption of a particle at a given site x, between times t and $t+\Delta t$, is

$$P[\eta_{t+\Delta t}(x) = 1 \mid \eta_t(x) = 0] = \lambda \Delta t + o(\Delta t),$$

where $\lambda \geqslant 0$ is the rate of birth at any site.

(1.3.2) The conditional probability of desorption of a particle at a given site x, between times t and $t+\Delta t$, is

$$P[\eta_{t+\Delta t}(x) = 0 \mid A_p(t, x)] = \mu_p \Delta t + o(\Delta t),$$

where the conditioning event $A_p(t, x)$ is "At time t, x is occupied and its neighborhood pattern is p.", so that $\mu_p \geqslant 0$ is the rate of death of a particle in pattern p.

(1.3.3) If p and p' are two neighborhood patterns such that p' is obtained from p by adding a molecule on a free site, then $\mu_p \geqslant \mu_{p'}$.

Hypothesis (1.3.1) is equivalent to assuming that the interval of time between a desorption and the following adsorption at one given site has an exponential distribution with constant parameter. This is the case if we suppose that the particles, present in large concentration in the solution, strike the surface randomly, according to a Poisson process of rate Λ. Then the interval of time for the adsorption to occur at a given site is exponential with parameter $\lambda = \Lambda/N$.

Hypothesis (1.3.2) amounts to saying that the interval of time before a desorption at a given site is an exponential random variable with parameter μ_p, depending on the neighborhood pattern of the site. It can also be seen as the duration of life on the surface of a particle in pattern p and its expected value is $1/\mu_p$. Therefore, the monotonicity relation imposed by (1.3.3) accounts for the intuitive idea that the more a particle is surrounded by others, the more stable is its state, and thus the harder it is for the particle to desorb. This hypothesis makes our system what is usually called an *attractive spin system*, and (see Section 3) it is an equivalent of an *attractive adsorbate-adsorbate interaction*. Not only does it correspond to a physical reality, but also it is most useful from a theoretical point of view.

Let us consider the case where all the rates μ_p are equal to μ. Then all the sites are independent. If n particles are present at a given time on the surface, then the interval of time before the next desorption is an exponential random variable with parameter $n\mu$. Hence, in this particular case, the number of particles present at one given time on the surface is the Markov process that has been studied in [22]. Its distribution at any instant of time and, virtually, every other variable associated with this model can be computed explicitly.

For other recent work on adsorption-desorption models see [23].

Remark. We assume that all quantities are non-dimensionalized with respect to the rate of adsorption λ. Multiplying each of the rates of birth c death by the same constant amounts to a simple change in the scale of time. Without loss of generality we may (and will) assume that the rate of birth λ is 1. Then our model has exactly as many effective parameters as neighborhood patterns.

2. THE MONTE-CARLO EXPERIMENTS

2.1. Parameters studied. Simulation of Markov processes such as described in 1.3 is a standard procedure and has already been used for different types of models (see [12] and [5]). The usual starting point is to simulate η_t, the evolution of the whole configuration with respect to time, but one of our aims was to select a few parameters that are easy to calculate and contain as much information as possible.

We chose to focus on the study of the distribution of occupied and empty sites in different neighborhood patterns. For each neighborhood pattern p, we denote by $m_p^1(t)$ (resp., $m_p^0(t)$) the number of occupied (resp., empty) sites in pattern of neighborhood p at time t. We show that these random variables convey all the information necessary to study both the evolution of coverage with respect to time and the clustering effect.

First, notice that the coverage of the surface at time t is given by the formula

$$\theta(t) = \frac{1}{N}\sum_p m_p^1(t), \tag{2.1.1}$$

where N is the total number of sites on the lattice. Of course, as far as the coverage current $I_\theta(t)$ is concerned, it is meaningless to differentiate $\theta(t)$ to obtain an estimate for $I_\theta(t)$. However, it is possible to construct an estimate directly from the m_p^1's and m_p^0's:

$$I_\theta(t) = \frac{1}{N}\left(\sum_p m_p^0(t) - \sum_p \mu_p m_p^1(t)\right). \tag{2.1.2}$$

To justify this, notice that between t and $t+\Delta t$, the curve $\theta(t)$ increases by $1/N$ with probability $\Delta t \sum_p m_p^0(t)$ (remember that $\lambda = 1$). It decreases by $-1/N$ with probability $\Delta t \sum_p \mu_p m_p^1(t)$. Hence formula (2.1.2) is an estimator of the expected slope of $\theta(t)$ at time t.

To quantify the clustering effect, many choices are possible: from studying correlations between sites [5] to counting the number of clusters of fixed size or evaluating the size of the biggest [12]. We propose to do this quantification by measuring the degree of dependence of the occupation of a site on its

neighborhood pattern. Let us define the function $S_c(t)$ by the formula

$$S_c(t) = -\sum_p \frac{m_p^1(t)+m_p^0(t)}{N}\left(\frac{m_p^1(t)}{m_p^1(t)+m_p^0(t)}\operatorname{Log}\frac{m_p^1(t)}{m_p^1(t)+m_p^0(t)} + \frac{m_p^0(t)}{m_p^1(t)+m_p^0(t)}\operatorname{Log}\frac{m_p^0(t)}{m_p^1(t)+m_p^0(t)}\right),$$

with the usual convention that $0\cdot\log 0 = 0$. This function represents the conditional entropy of the distribution of occupied sites with respect to the distribution of sites in different patterns.

It can be proved easily ([4], Chapter 10) that the above conditional entropy is a non-negative number verifying the inequality

$$S_c(t) \leqslant -\theta(t)\log\theta(t) - (1-\theta(t))\log(1-\theta(t)),$$

with the equality taking place if and only if the occupation of a site is independent of its neighborhood pattern. On the contrary, in the extreme case of a completely clustered configuration, most of sites are either occupied with all neighbors occupied or empty with all neighbors empty, and the quantity $S_c(t)$ is then close to zero. Thus it is natural to choose

$$S(t) = S_c(t)/\big(-\theta(t)\log\theta(t) - (1-\theta(t))\log(1-\theta(t))\big) \tag{2.1.3}$$

as a measure of the clustering effect. $S(t)$ will be called here the *standardized conditional entropy*. It satisfies the inequalities $0 \leqslant S(t) \leqslant 1$, and the smaller $S(t)$ is, the more clustered the configuration at time t becomes.

Another interesting aspect of the clustering effect is that the clusters may be not only of different sizes but also of different shapes. In order to take into account the degree of intricacy of those shapes, we chose to study the following estimates of the total length of the border between occupied and unoccupied sites:

$$L(t) = \frac{1}{2}\sum_p m_p^1(t)(4-n(p)) + \frac{1}{2}\sum_p m_p^0(t)(n(p))$$

in the case of the square lattice, and

$$L(t) = \frac{1}{2\sqrt{3}}\sum_p m_p^1(t)(6-n(p)) + \frac{1}{2\sqrt{3}}\sum_p m_p^0(t)(n(p))$$

in the case of the triangular lattice. In both expressions, $n(p)$ is the number of occupied neighbors of a site in pattern p.

Of course, lengths of the border can be compared only for two configurations having the same coverage. In order to compare lengths at different coverages, we define $C(t)$ by the formula

$$C(t) = \frac{\operatorname{Log}(L(t))}{\operatorname{Log}(N\cdot\theta(t))}. \tag{2.1.4}$$

Quantity $C(t)$ can be regarded as a measure of complexity of the border of clusters, and is closely related to the notion of ε-entropy of a curve (cf. [18]

2.2. Computer experiments. The simulation (run on a DEC PRO 350 microcomputer) takes place on a rectangular lattice of size $N \times (N+1)$. The abscissa (resp., ordinate) of a site is an element of the set of integers modulo N (resp., $N+1$). We establish a one-to-one correspondence between the set of sites and the set of integers modulo N^2+N. To a site of coordinates (x, y) there corresponds

$$k = (N+1)x - Ny \ (\text{Mod } N^2+N).$$

The inverse of this mapping assigns the site with coordinates (k (Mod N), k (Mod $N+1$)) to the integer k. This allows us to store each configuration of sites in a one-dimensional vector with N^2+N Boolean coordinates. Associated with each site is a Boolean vector representing its neighborhood pattern. Suppose that the current configuration is such that the numbers of occupied and empty sites in neighborhood pattern p are m_p^1 and m_p^0, respectively. Then the next event to occur will be either an adsorption with probability

$$(\sum_p m_p^0)/(\sum_p m_p^0 + m_p^1 \mu_p)$$

or a desorption at an occupied site in pattern p with probability

$$m_p^1 \mu_p / (\sum_p m_p^0 + m_p^1 \mu_p).$$

All adsorptions (resp., all desorptions at a site in pattern p) have equal probabilities. The choice of the next event is decided by the generation of a pseudo-random number, using a generator of a convergence type:

$$g(x) = (2^{15}+5)x + 1 \ (\text{Mod } 2^{29}).$$

Then the program scans the vector of sites to find the coordinate corresponding to the event that has been decided. It reactualizes the status of this coordinate and the patterns of its neighbors. Finally, the scale of dimensionless time is increased by

$$\Delta t = (\sum_p m_p^0 + m_p^1 \mu_p)^{-1}.$$

Rigorously it should be increased by a random number generated according to an exponential random variable with average Δt. We believe that this approximation does not influence the results.

For a given set of rates $\{\mu_p\}$ and a size of the lattice, we first determine a value T representing the time when it can be assumed (approximately) that the coverage has reached its asymptotic value. Then the interval of time $[0, T]$ is divided into 100 intervals by the instants $t_i = i(T/100)$, $i = 1, \ldots, 100$.

The experiment consists of running the program of simulation, starting from an empty lattice at $t = 0$ until the scale of time reaches the value T. For each instant t_i the program computes the quantities $\theta(t_i)$, $I_\theta(t_i)$, $S(t_i)$, $C(t_i)$,

using the formulas (2.1.1)–(2.1.4). So the result of one experiment is a file of 100×4 data.

For each set of parameters, the experiment described above is repeated 30 times. Then another program uses the 30 data files so created to compute the averages and standard deviations of the four quantities we want to study for each of the instants t_i. The final result is a file of 100×8 data. Another program plots these data, which permits their comparison.

Some of the results we observed were to be expected. For instance, we ran an experiment with all rates of death being equal, and the results fit the prediction of [22] with very good levels of confidence. However, other results were less expected and quite intriguing. In particular, it turned out that, for comparable rates, the behavior of the models on the square lattice and the triangular lattice were remarkably alike (see Fig. 2 for an illustration of this). Another interesting feature was that radical changes that can be observed in the behavior of the coverage current when the range of rates is expanded. The graph of $I_\theta(t)$ changes from a convex, exponentially decaying, type of curve to a curve with a much more irregular behavior, such as the one observed in Fig. 2.

The range of values for the rates of desorption also influences the clustering effect. For instance, when the rate of death of a particle is 100 if it is isolated and less than 1 in any other case, then very few isolated particles tend to remain on the lattice. Such a situation is illustrated in Figs. 3 and 4, which

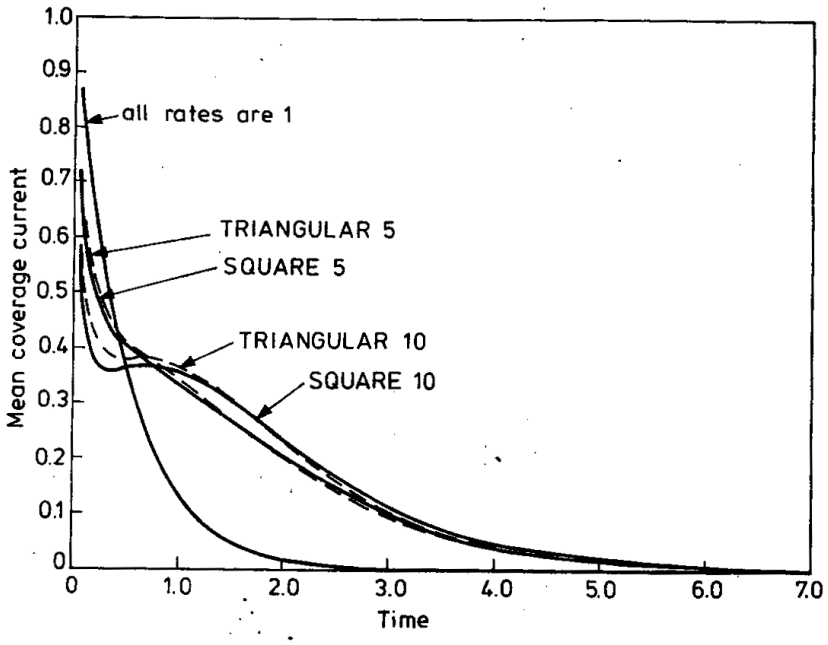

Fig. 2. *Mean coverage current* ($I_\theta(t) = d\theta(t)/dt$) *as a function of time assuming a wide range of death rates.* The rate of death μ_p in pattern p (for both square and triangular lattices) corresponding to different curves is indicated on the graph. TRIANGULAR 5 means that $\mu_p = 5^{(-2/3)n(p)+1}$, SQUARE 5 is for $\mu_p = 5^{-n(p)+1}$, TRIANGULAR 10 is for $\mu_p = 10^{-(2/3)n(p)+1}$, and SQUARE 10 is for $\mu_p = 10^{-n(p)+1}$. μ_p depend only on the number $n(p)$ of occupied neighbors of a site in pattern p. The exponential curve corresponding to the case of independent sites is given for comparison. For all experiments described in this paper the total number of sites on the lattice was 10100. Also, all the quantities are non-dimensionalized with respect to the rate of adsorption λ

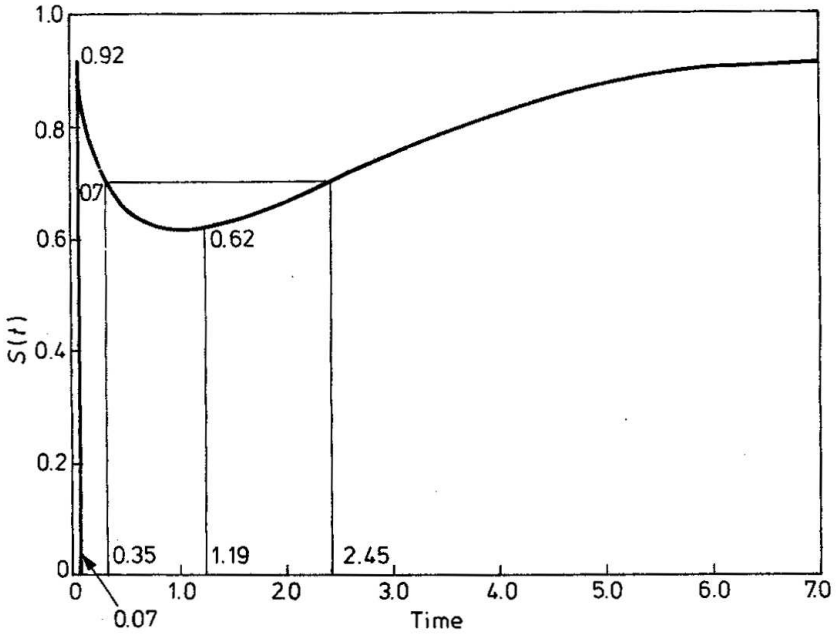

Fig. 3. *Mean standarized conditional entropy* $S(t)$ (cf. (2.1.3)) *as a function of time assuming a narrow range of death rates.* This curve corresponds to a simulation on the square lattice, the rate of desorption being 100 for an isolated particle and $\mu_p = 1-0.2n(p)$ for a particle with $n(p)$ neighbors ($n(p) \geqslant 1$)

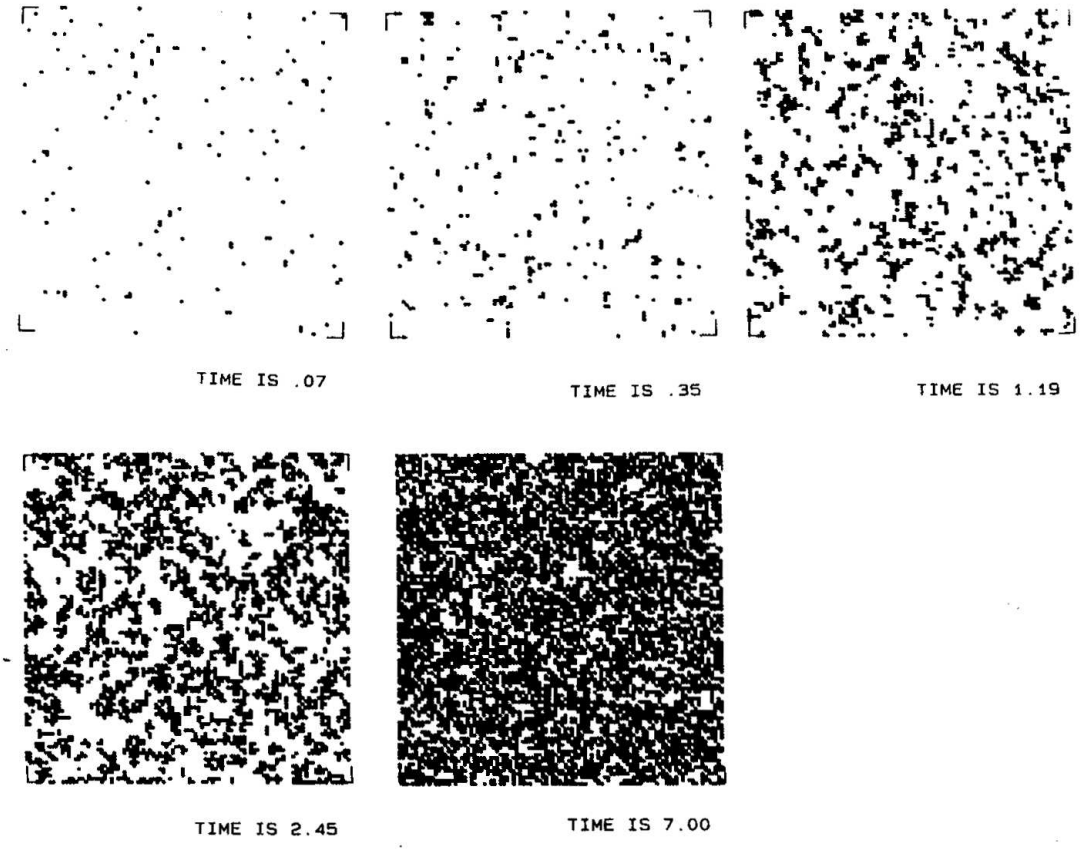

Fig. 4. Actual configurations of occupied sites at different instants of time for a simulation on the square lattice with the same rates as for Fig. 3. At each of the five instants of time the appearance of the grid should be compared with corresponding values of the function $S(t)$ on Fig. 3, which measure the degree of clustering in a given configuration

compare the quantitative behavior of the conditional entropy $S(t)$ with the aspect of the grid at corresponding times. Finally, an interesting type of behavior was observed for the quantity $C(t)$, measuring the complexity of the shapes of clusters. It decreases almost linearly with time, with a slope depending on the range of values for the rates of death (Fig. 5).

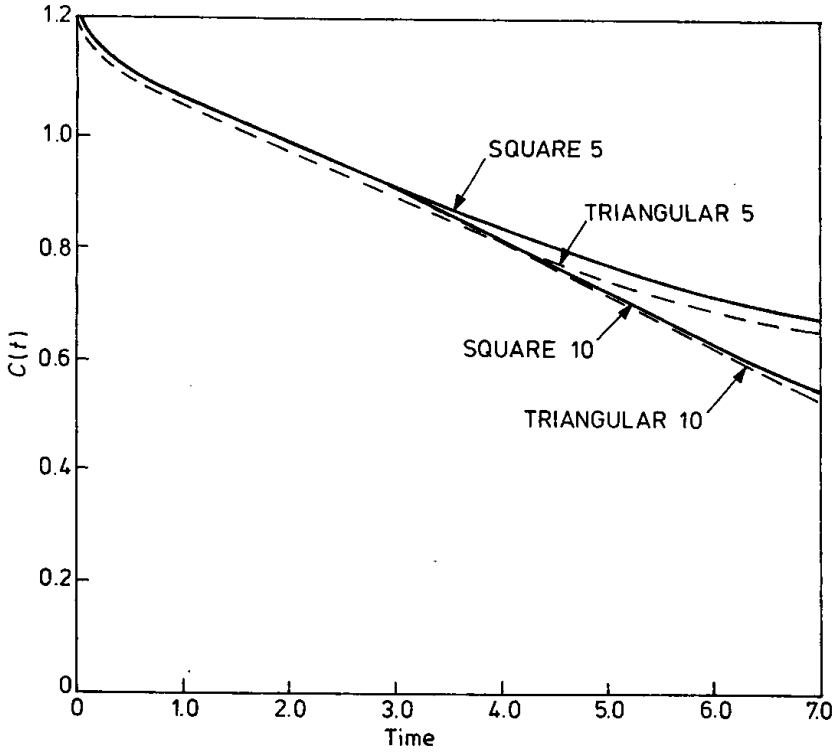

Fig. 5. *Mean complexity of clusters* as measured by $(\log L(t))/\mathrm{Log}(N\cdot\theta(t))$, where $L(t)$ is the length of the border between occupied and empty sites and $N\cdot\theta(t)$ is the number of occupied sites at time t. The four curves correspond to the same experiments as those in Fig. 2. It is worth noticing that the curves corresponding to the triangular lattice (dashed line) decrease slightly more rapidly than the curves corresponding to the square lattice. This indicates that the clusters in the triangular lattice tend to be more regular than in the square lattice for a comparable set of parameters

2.3. Conclusion. The results are not sufficient to draw very general conclusions; the simulations were limited by the capacity of the computer. However, the experiments showed such a diversity of behaviors that at a very early stage we felt a need to reduce our study to particular choices of the parameters μ_p. It is also possible, but cumbersome, to estimate these rates by a quantum mechanical computation of the global energy of different patterns of neighborhood for specific choices of the surface net (e.g., Pt(110)) and adsorbate (e.g., Pb). Another possibility that would go one step further than the Ising model (cf. Section 3.4) would be to consider that some harmonic forces of interaction are superposed on top of the forces of attraction between particles. This would lead to the rates of death of the form

$$\mu_p = \mu h^{n(p)}(n(p)+1)^{1/2},$$

where $\mu > 0$, $0 < h \leqslant 1$, and $n(p)$ is the number of occupied neighbors of a site in pattern p.

3. THEORETICAL RESULTS

3.1. Definitions. The model presented here is a particular case of spin systems, the theory of which is itself imbedded in the general framework of interacting particle systems.

Let S be a countable set of sites, and $X = \{0, 1\}^S$ the set of all possible configurations of those sites. A *spin system* is a Markov process on X such that, in a small interval of time, the current configuration can be changed (flipped) at only one site, the rate of occurrence of this flip depending on the site and the configuration.

Let η_t be the current configuration at time t, and x a site ($\eta_t(x)$ is the status, 0 or 1, of the site x at time t). Then

$$P[\eta_{t+\Delta t}(x) \neq \eta_t(x) \mid \eta_t = \eta] = c(x, \eta)\Delta t + o(\Delta t).$$

The coefficients $c(x, \eta)$ are called the *rates of flip* of the spin system. When $\eta(x) = 0$ (resp., $\eta(x) = 1$), $c(x, \eta)$ can be interpreted as the *rate of birth* (resp., *death*) at site x.

Since in our case the rates of flip $c(x, \eta)$ for each x depend only on a finite number of coordinates of η, the Markov process η_t exists (cf. [17], Chapter III).

When S is finite, the set of configurations X is also finite, and it is a consequence of a well-known result that then any spin system on X is *ergodic*, i.e., it admits a unique invariant measure and the process converges in law to this measure, regardless of initial distribution (cf., e.g., [14]). When S is infinite, this is no more the case: even some very simple models (e.g., the stochastic Ising models) may not be ergodic. Physically, the lack of ergodicity permits first order phase transitions.

Apart from a few particular cases, even for relatively simple models, the theory of spin systems is quite difficult, which justifies a use of the Monte-Carlo simulation techniques. However, some theoretical results about spin systems exist and are useful for our purposes. We describe them in the following sections. Section 3.2 is devoted to the Comparison Theorem. We first use it to provide two-sided estimates for the evolution of the coverage function with respect to time (Proposition 3.2.3). Another important consequence of the Comparison Theorem is Theorem 3.2.5 that describes the asymptotic behavior of an attractive spin system. The constant process and the stochastic Ising model are two important particular cases of our model (Sections 3.3 and 3.4) and the Comparison Theorem can also be used to extend some results already known for those particular processes (Propositions 3.3.1 and 3.3.3).

3.2. The Comparison Theorem. We first proceed to define a partial order between measures on the set of configurations X. X itself is naturally endowed with a *partial order* by

$$\eta \leqslant \zeta \Leftrightarrow \eta(x) \leqslant \zeta(x), \ \forall x \in S.$$

This, in turn, yields the notion of a monotone function on X: f is *monotone* if and only if

$$(\eta \leqslant \zeta \Rightarrow f(\eta) \leqslant f(\zeta),\ \forall \eta, \zeta \in X).$$

Let $\mathcal{M}$ be the set of those functions on X which are both continuous and monotone: the prototype of functions in $\mathcal{M}$ is the function counting the number of occupied sites inside a given finite set.

DEFINITION 3.2.1. Let ν_1 and ν_2 be two measures on X. We shall say that $\nu_1 \leqslant \nu_2$ if

$$\int f d\nu_1 \leqslant \int f d\nu_2,\ \forall f \in \mathcal{M}.$$

To interpret this definition, let us notice that if ν_1 and ν_2 are probability measures on X and $\nu_1 \leqslant \nu_2$, then the average number of occupied sites in any finite set is smaller for ν_1 than for ν_2.

The basic tool for our study is the following theorem. Its proof (omitted here) is an application of coupling techniques and can be found in Chapter III of [17].

COMPARISON THEOREM 3.2.2. *Let $c_1(x, \eta)$ and $c_2(x, \eta)$ be the rates of two spin systems satisfying the following condition: if $\eta \leqslant \zeta$, then*

$$c_1(x, \eta) \leqslant c_2(x, \zeta) \quad \text{if } \eta(x) = \zeta(x) = 0,$$
$$c_1(x, \eta) \geqslant c_2(x, \zeta) \quad \text{if } \eta(x) = \zeta(x) = 1.$$

Let $\{S_1(t), t \in [0, \infty[\}$ and $\{S_2(t), t \in [0, \infty[\}$ be the semigroups of these spin systems and let ν_1 and ν_2 be two measures on X such that $\nu_1 \leqslant \nu_2$. Then

$$\nu_1 S_1(t) \leqslant \nu_2 S_2(t) \quad \text{for all } t \geqslant 0.$$

Interpretation. If ν is the initial distribution of η_0, and $\{S(t)\}$ the semigroup of a spin system, then $\nu S(t)$ is the distribution of the process at time t. Now, assumption (*) means that when $\eta \leqslant \zeta$, the rate of birth (resp., death) at any site of the first spin system is smaller (larger) than for the second one. The logical conclusion is that if the first spin system starts with a deficit in occupied sites, this deficit will never be erased.

In our case, as an immediate consequence of the above theorem, we can provide upper and lower bounds for the mean coverage $\mathrm{E}(\theta(t))$ at time t.

PROPOSITION 3.2.3. *Consider the spin system defined in Section* 1.3. *Let μ_0 (resp., μ_1) be the rate of death in the empty (resp., full) neighborhood pattern. Let $\theta(t)$ be the coverage (proportion of occupied sites at time t) and $\mathrm{E}(\theta(t))$ its mathematical expectation. If at time $t = 0$ the configuration is empty, then, for all $t \geqslant 0$,*

$$\frac{\lambda}{\lambda+\mu_0}(1-\exp[-(\lambda+\mu_0)t]) \leqslant \mathrm{E}(\theta(t)) \leqslant \frac{\lambda}{\lambda+\mu_1}(1-\exp[-(\lambda+\mu_1)t]).$$

Proof. Hypothesis (1.3.3) implies that, for any pattern p, the corresponding rate of death μ_p satisfies $\mu_1 \leqslant \mu_p \leqslant \mu_0$. Let us define the rates $c_i(x, \eta)$, $i = 1, 2$, by

$$c_1(x, \eta) = \begin{cases} 1 & \text{if } \eta(x) = 0, \\ \mu_0 & \text{if } \eta(x) = 1, \end{cases}$$

$$c_2(x, \eta) = \begin{cases} 1 & \text{if } \eta(x) = 0, \\ \mu_p & \text{if } \eta(x) = 1, \end{cases}$$

and the neighborhood pattern of x is p. Now, one can apply the Comparison Theorem to c_1 and c_2, with ν_1 and ν_2 equal to the Dirac mass on the empty configuration. As the proportion of occupied sites is a monotone function, its average value is less for the first spin system than for the second one. But in the first spin system, the rates do not depend upon the configuration, so that the sites may be considered as independent. As we already proved in [22], the mean coverage in this case is equal to

$$(\lambda/(\lambda+\mu_0))(1-\exp[-(\lambda+\mu_0)t]).$$

Hence the first inequality holds. The second inequality is obtained in an analogous fashion.

The Comparison Theorem is especially important in the case of so-called attractive spin systems.

DEFINITION 3.2.4. A spin system with rates $c(x, \eta)$ is said to be *attractive* if assumption (*) is satisfied by $c_1(x, \eta) = c_2(x, \eta) = c(x, \eta)$.

One checks easily that assumption (1.3.3) is the translation of the above definition to our particular case.

The next theorem describes principal properties of attractive spin systems. They are direct consequences of the Comparison Theorem. The notation δ_0 (resp., δ_1) designates the Dirac mass on the empty (resp., full) configuration.

THEOREM 3.2.5. *Let* $\{S(t), t \in \mathbf{R}^+\}$ *be the semigroup of an attractive spin system. Then*:

(a) $\delta_0 S(s) \leqslant \delta_0 S(t)$ *for* $0 \leqslant s \leqslant t$;

(b) $\delta_1 S(s) \geqslant \delta_1 S(t)$ *for* $0 \leqslant s \leqslant t$;

(c) $\delta_0 S(t) \leqslant \mu S(t) \leqslant \delta_1 S(t)$ *for* $t \geqslant 0$ *and any probability* μ;

(d) $\underline{\nu} = \lim_{t \to \infty} \delta_0 S(t)$ *and* $\bar{\nu} = \lim_{t \to \infty} \delta_1 S(t)$ *exist*;

(e) *if* μ *is a probability measure,* $t_n \to \infty$ *and* $\nu = \lim_{n \to \infty} \mu S(t_n)$, *then* $\underline{\nu} \leqslant \nu \leqslant \bar{\nu}$;

(f) $\underline{\nu}$ *and* $\bar{\nu}$ *are extreme points in the set of invariant measures.*

Interpretation. This theorem allows us to restrict our study by prescribing the starting point to be either the empty configuration or the full configuration: The two types of evolutions so obtained constitute, in some sense, lower and upper bounds for any other possible behavior (property (c)).

These two choices of the initial distribution have been taken into account in our simulation program. Moreover, in the infinite case, the comparison of the asymptotic measures $\underline{\nu}$ and $\bar{\nu}$ provides a simple criterion of ergodicity: The spin system is *ergodic* iff $\underline{\nu} = \bar{\nu}$.

Even more information can be derived from the monotone behavior described in (a) and (b): We already noticed that the mean coverage $E(\theta(t))$ is a monotone function. If the initial configuration is empty, then the mean coverage is an increasing function of time, and if the initial configuration is full, then the mean coverage is a decreasing function of time. As expected, this property was verified in the simulation (cf. Section 2.2).

3.3. The contact process. This process is a very important particular case of our model. It was introduced and first studied by Harris (cf. also [17], Chapter VI, and [11]). It is defined on the square lattice $\boldsymbol{Z}^2$ by the conditions: if $\eta(x) = 1$, $c(x, \eta) = 1$; and if $\eta(x) = 0$, $c(x, \eta) = nh$, where h is a positive constant, and n is the number of occupied neighbors of x. (Note that, formally, to consider the contact process as a particular case of our model, one has to reverse the roles of 0 and 1.) The main result in the theory of contact processes is the existence of a critical value h_c such that the contact process is ergodic for $h < h_c$ and is not ergodic for $h > h_c$. Computing the exact value of h_c is usually a difficult problem. The best rigorous result known in this direction seems to be the estimate $1/3 < h_c < 1$. The existence of a critical value for the contact process allows us, through the Comparison Theorem, to construct conditions for ergocity of a particular case of our model:

PROPOSITION 3.3.1. *Suppose the rates of a spin system are defined as in Section* 1.3, *on the square lattice, with* $\mu_1 = 0$. *Let* $\bar{h}$ *and* $\underline{h}$ *be defined by*

$$\bar{h} = \operatorname{Inf}\{h \in \boldsymbol{R} \mid \mu_p \leqslant h(4 - n(p))\}, \qquad \underline{h} = \operatorname{Sup}\{h \in \boldsymbol{R} \mid \mu_p \geqslant h(4 - n(p))\},$$

where $n(p)$ *is the number of occupied neighbors in pattern* p. *Then, if* $\bar{h} < h_c$, *the spin system is ergodic, and if* $\underline{h} > h_c$, *the spin system is not ergodic.*

Proof. The hypothesis $\mu_1 = 0$ implies that the system considered above admits δ_1, the Dirac mass on the full configuration, as an invariant measure. If we reverse the roles of 0 and 1, so does the contact process. Now suppose that two systems having δ_1 as an invariant measure verify assumption (*) of the Comparison Theorem. If the first one is ergodic, then for any initial distribution ν we have

$$\lim_{t \to \infty} \nu S_1(t) = \delta_1.$$

Then, since $\nu S_1(t) \leqslant \nu S_2(t) \leqslant \delta_1$ for all t, we also have

$$\lim_{t \to \infty} \nu S_2(t) = \delta_1,$$

and the second system is also ergodic.

The importance of the previous proposition is enhanced by the following transformation, which turns any spin system into an attractive spin system with δ_0 as an invariant measure.

If $c(x, \eta)$, $x \in S$, $\eta \in X$, are the flip rates for a spin system, then define new flip rates by

$$\bar{c}(x, \xi) = \mathrm{Sup}\{|c(x, \eta) - c(x, \zeta)|: |\eta(w) - \zeta(w)| \leqslant \xi(w) \text{ for all } w \in S\} \quad \text{if } \xi(x) = 0,$$

$$\bar{c}(x, \xi) = \mathrm{Inf}\{[c(x, \eta) + c(x, \zeta)]: \eta(x) \neq \zeta(x) \text{ and } |\eta(w) - \zeta(w)| \leqslant \xi(w) \text{ for all } w \in S\} \quad \text{if } \xi(x) = 1.$$

PROPOSITION 3.3.2. *If the process ξ_t corresponding to $\bar{c}(x, \xi)$ is ergodic, then so is the process η_t corresponding to $c(x, \eta)$.*

This transformation and the proof of Proposition 3.3.2 can be found in [17], Chapter III.

In our particular case, where the rates $c(x, \eta)$ are defined as in Section 1.3, the transformation gives rates of a similar type, the roles of 0 and 1 being exchanged: if $\xi(x) = 1$, $\bar{c}(x, \xi) = 1 + \mu_1$; if $\xi(x) = 0$, $\bar{c}(x, \xi) = \bar{\mu}_p$, where $\bar{\mu}_p$ depends upon the neighborhood pattern p of x in configuration ξ.

Coupling Propositions 3.3.1 and 3.3.2 yields the following general sufficient condition of ergodicity for our model.

PROPOSITION 3.3.3. *Let $\bar{h} = \mathrm{Inf}\{h \in \mathbf{R} \mid \bar{\mu}_p \leqslant h(4 - n(p))\}$. If $\bar{h}/(1 + \mu_1) < h_c$, then the model with rate of birth equal to 1 and rates of death μ_p is ergodic.*

However, this condition is not necessary as is shown in the example of the spin systems defined in Section 1.3 with rates μ_p additionally verifying the condition

$$\mu_p = \mu + h(4 - n(p))$$

for some non-negative μ and h. The coalescing duality argument ([17], Chapter III) shows that this spin system is ergodic for any h as long as $\mu > 0$. Transforming it by a method described above gives the contact process with parameter $h/(1 + \mu)$. Note that this example can be seen as a particular case of a voter model with defections as defined in [7], Section 4.

3.4. The stochastic Ising model. The stochastic Ising model is in a sense the best known and the simplest of all classical particle systems. One of its characterizations is that it is a spin system with positive rates, which is reversible with respect to some measure on X. Proofs of results we are listing here can be found in [17], [7] or [16] (the latter focusing on the connections with Gibbs states and Markov fields).

In this section we consider a spin system defined in Section 1.3, with the rates of death μ_p satisfying the condition $\mu_p = \mu \cdot h^{n(p)}$ for some $\mu > 0$ and $0 < h \leqslant 1$, where $n(p)$ is the number of occupied neighbors of a site in pattern p.

In the usual terminology (cf. [17]), this system is a *stochastic Ising model* associated with the potential J defined on subsets of the set of sites S by the formulas

$$J(\{x\}) = \mathrm{Log}(\mu h^2),$$

$$J(\{x, y\}) = kT/2\log h \quad \text{if } x \text{ and } y \text{ are neighbors,}$$

$$J(R) = 0 \quad \text{for any other subset } R \text{ of } S.$$

The model admits as a reversible (and thus invariant) measure, the Gibbs states corresponding to the same potential. Thus the ergodicity of this spin system is linked to the absence of phase transition for the corresponding potential.

We summarize in the following theorem the classical results relative to the ergodicity of this model.

THEOREM 3.4.1. *If $\mu h^2 \neq 1$, then the model is ergodic. If $\mu h^2 = 1$, then it is ergodic iff*

$$\tfrac{1}{2}\log h \leqslant \beta_0 = \tfrac{1}{2}\mathrm{Arcsinh}(1).$$

If the system is not ergodic, then any invariant measure ν is a convex combination of

$$\underline{\nu} = \lim_{t\to\infty} \delta_0 S(t) \quad \text{and} \quad \bar{\nu} = \lim_{t\to\infty} \delta_1 S(t)$$

(cf. Theorem 3.2.5).

A Monte-Carlo study of both transient and asymptotic behaviors of some stochastic Ising models on the square lattice has already been conducted by Hammersley and Mazzarino [12].

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