Journal of Statistical Physics, Vol. 70, Nos. 5/6, 1993

A Stochastic Model of Deposition Processes with Nucleation

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Received April 23, 1992; final September 24, 1992

We study an interacting particle system on a one-dimensional infinite lattice and one-dimensional lattices with a periodic boundary. In this system, each site of the lattice may be either empty or occupied and initially all the lattice sites are empty. The evolution of the system is defined as follows: an empty site waits an exponential time with mean 1 and becomes occupied, and an occupied site becomes empty at a time which is distributed exponentially with mean μ_k, where k is the number of occupied neighboring sites of this site in the current state of the system. We show that the mean number of the occupied sites of the lattice, considered as a function of time, may possess a convex part. A sufficient condition for this is that μ_0 is large and μ_k, $k \geqslant 1$, are small. The studied system has been proposed recently as a mathematical model of certain deposition processes, in particular those which exhibit nucleation caused by lateral attractive interaction between the deposited molecules. Our research was motivated by the observation that the density of deposited molecules contains a convex part, over some time interval, if the attractive forces are strong, while this density is a concave function of time if these forces are weak or absent. Our result agrees with this observation.

KEY WORDS: Interacting particle systems; modeling of initialization and growth of nuclei; dynamical behavior.

1. INTRODUCTION

Let G be an infinite one-dimensional lattice or a finite one-dimensional lattice with a periodic boundary. Each site of the lattice can be either occupied (by a particle) or empty. By φ_t, $t \geqslant 0$, we denote a time-homogeneous stochastic process which evolves on the set of all configurations of empty and occupied sites of G according to the following rules. Assume that a configuration at which the process stays at time $t \geqslant 0$ is

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0022-4715/93/0300-1233$07.00/0

given; we then define that: (i) a site which is empty in this configuration will become occupied at time $t+\Delta t$ with probability $\Delta t + o(\Delta t)$ (this event is called an *adsorption* of a particle at the site); (ii) a site which is occupied and has k occupied neighbors in the given configuration will become empty at time $t+\Delta t$ with probability $\mu_k \Delta t + o(\Delta t)$ (this event is called a particle's *desorption*); (iii) the probability that more than one site change their states within time interval Δt is $o(\Delta t)$; we also assume (iv) $\mu_0 \geqslant \mu_1 \geqslant \mu_2$ and (v) initially, the process start from $\varnothing$, where $\varnothing$ denotes the configuration in which all sites are empty. The process φ_t, $t \geqslant 0$, which satisfies (i)–(v) will be called *an adsorption–desorption process* (ADP). A particular case of ADP for which $\mu_0 = \mu > 0$ and $\mu_k = 0$, $k \geqslant 1$, is called *a sticking process*; it will be denoted by ϕ_t, $t \geqslant 0$.

Let us denote by $\rho(t)$ the probability that a particular site of G, say the site 0 for concreteness, is occupied in an ADP at time t. The function $\rho(t)$, $t \geqslant 0$, will be called *the density function*; it expresses the average density of the occupied sites of G considered as a function of time. A condition on the parameters $\mu_0, \ldots, \mu_s$ which implies that $\rho(t)$ is concave for all $t \geqslant 0$ is known.[3] In this paper, we give a condition for the density function to possess a convex part, over some time interval. We establish (Theorem in Section 2) that if the *size* of G, that is, the number of the sites in G, exceeds 7 (including the case when G is infinite), then the density function of a sticking process satisfies

(A) $(d^2/dt^2)\, \rho(2(\ln \mu)/\mu) > 0$ for all $\mu > \bar{\mu}$

(B) $(d^2/dt^2)\, \rho((\ln \mu)/\mu) < 0$ for all $\mu > \mu^*$

where $\bar{\mu}$ and μ^* are finite constants independent of the size. Assuming there is only one convex part in the density function, (A) and (B) give an estimate on the time coordinate of the first inflection point. A computer simulation[2] shows that the density function of the sticking process possesses a convex part also when G is a torus in $\mathbb{Z}^2$. However, in this case or that of other, more complicated structures of G, our method requires the calculation of a huge (although finite) number of multiple integrals. Neither would we be able to do this by hand, nor would it be possible to present the results in the form of a short article. However, we hope our method works for these cases as well, and we intend to realize it with the help of symbolic calculation programs. It is appropriate to mention that a result similar to (A) has been reported by Granovsky *et al.*[6] for the case when the size of G equals 3. The method used in ref. 6 is based on solving a system of differential equations and is unlikely to be applicable for big lattices.

It is easy to show that the sticking process is not the only representative of the ADPs which has a nonconcave density function. A par-

ticularly interesting case is when an ADP is reversible with respect to its invariant measure. In this case, the ADP is equivalent to a particular stochastic Ising model (in Section 2, we specify this equivalence; for the definition of the stochastic Ising model and related concepts, we refer the reader to ref. 10, Chapter IV). The corollary in Section 2 gives a sufficient condition for the density function of a reversible ADP to possess a convex part. Being interpreted in the terms of the stochastic Ising model, this corollary says: Let $\zeta(t;\beta)$, $t\geqslant 0$, be a stochastic Ising model on a torus in $\mathbb{Z}^1$ which relates to the translation-invariant symmetric nearest-neighbor potential $J_1:=\beta H$, $J_2:=\beta>0$, where H is connected to β through $2\beta(2-H)=C$ for some constant $C\geqslant \ln\bar{\mu}$. Assume that in this process, the flip rate from -1 to $+1$ equals 1 and the process starts from the configuration "all minuses." Then the magnetization of this process, considered as a function of time, possesses a convex part if β is sufficiently large.

The following qualitative explanation of a possible nonconcave shape of the density function has been suggested by Bernard Ycart (personal communications). For the case of the sticking process, a particle which has at least one neighboring particle on G will be stuck, i.e., unable to leave G. Recall that the lattice sites are empty initially. Thus, until the first event when any two particles get stuck, the sticking process behaves like a birth-and-death process whose rates of birth and death are 1 and $\mu_0=\mu$, respectively, and which starts from the configuration $\varnothing$. Thus, for small t, $\rho(t)$ would be close to the curve $\{1-\exp[-(1+\mu)t]\}/(1+\mu)$, which is the density function of this birth-and-death process. On the other hand, for large t, there are very few empty sites of the lattice, so that an adsorbing particle is unlikely to be isolated on G and therefore will never be desorbed. Thus, when t is large, $\rho(t)$ would be close to the curve $1-\exp(-t)$, that is, the density of the pure birth process whose birth rate is 1. If μ is large, so is the gap between these two curves. Consequently, the density function of the sticking process will be unable to pass from one curve to another "smoothly," but rather will have to "accelerate" at a certain stage that would be expressed in breaking the concavity. The idea of comparing ϕ_t with a birth-and-death process is the basis of the proof of (A) and (B) and, with some additional technique, provides a comprehensive explanation of the nonconcavity to be presented at the end of the next section.

The adsorption–desorption process has been recently suggested[14, 13] as a model of a deposition process called *underpotential deposition* (UPD). Actually, ADP was proposed to describe UPD accounting for the lateral interaction between the deposited ions. Ref. 9 reviews the state of knowledge of UPD up to 1976, and the nucleation phenomenon in UPD which indicates the presence of lateral attractive forces between the deposited ions is discussed, e.g., in ref. 8. Refs. 11, 12, and 5 contain a

mathematical investigation of this phenomenon. We would like to remark that the mathematical models of initialization and growth of nuclei proposed in these papers can be regarded, to a certain extent, as particular cases of ADP.

Our interest in the nonconcave behavior of the density function of the ADP was motivated by ref. 6, which reported that for a certain deposition process, the analogue of the density function may possess a convex part, over some time interval. The results presented in ref. 6 were obtained by processing the experimental data provided by Hansen and Wallace[7] regarding the determination of the dependence of the surface tension of various aqueous solutions on concentration and time. For the process of creation of the solution–air interface, which is the process studied in ref. 7, the analogue of the density function is called the *excess*; it is usually denoted by Γ; let us also introduce the *surface coverage parameter* $\theta_{eq} := \Gamma(\infty)/\Gamma_{max}$, where $\Gamma(\infty)$ corresponds to the value of the excess in the equilibrium state for a given concentration of surfactant, and Γ_{max} is the maximum in the isotherm of $\Gamma(\infty)$ versus concentration (see ref. 1 for background). After the transformation of the original tension-versus-time data to data which relate the excess to time, the following difference in the behavior of the aqueous solutions of pentanoic and octanoic acids was observed. For pentanoic acid, $\Gamma(t)$ is a concave function of time for all values of θ_{eq}. On the other hand, for octanoic acid, if the value of θ_{eq} is close to one, then the excess, considered as a function of time, will possess a convex part. It is known that octanoic acid molecules, being longer than those of pentanoic acid, interact more strongly because the strength of intermolecular forces between straight-chain carboxylic molecules increase with chain length. In the studied process, the existence of lateral interaction is substantiated by the violation of the Langmuir law observed for octanoic acid (see ref. 1 for the derivation of the Langmuir isotherm for a lattice gas). Thus, the difference in the dynamics of the excess for octanoic and pentanoic acids may be explained by lateral interaction between molecules in the solution–air interface. The result presented in this paper agrees with this explanation.

2. DEFINITIONS AND RESULTS

The adsorption–desorption process (ADP) investigated in this paper is a particular interacting particle system. Ref. 10 is the best reference for the theory of IPS; the construction of ADP presented below follows this book.

Throughout this section, G denotes a one-dimensional infinite lattice (usually designated by $\mathbb{Z}^1$ in the mathematical literature) or a one-dimen-

sional finite lattice with a periodic boundary (called also a torus in $\mathbb{Z}^1$). We will use the same symbol G to denote the set of all sites of the lattice G.

A function $\eta: G \to \{0; 1\}$ is called *a configuration.* The set of all configurations on a lattice G is denoted by $\mathscr{X} := \{0; 1\}^G$. A site $x \in G$ is called *occupied* in a configuration $\eta \in \mathscr{X}$ if $\eta(x) = 1$ and *empty* if $\eta(x) = 0$. For $x \in G$ and $\eta \in \mathscr{X}$, we define a new configuration η_x, called the configuration η flipped at x, in the following way:

$$\eta_x(y) = \begin{cases} 1 - \eta(x) & \text{if} \quad y = x \\ \eta(y) & \text{otherwise} \end{cases} \qquad \text{for all} \quad y \in G$$

Let $\mathscr{C}(\mathscr{X})$ denote the set of continuous functions acting from $\mathscr{X}$ to $\mathbb{R}$ and let $L(\mathscr{X}) \subseteq \mathscr{C}(\mathscr{X})$ be the set of cylinder functions. Define a linear operator $\mathscr{G}: L(\mathscr{X}) \to \mathscr{C}(\mathscr{X})$ by virtue of the following formula:

$$(\mathscr{G}f)(\eta) := \sum_{x \in G} c(x, \eta)[f(\eta_x) - f(\eta)], \qquad \eta \in \mathscr{X} \tag{1}$$

where

$$c(x, \eta) := \begin{cases} \lambda \equiv 1 & \text{for} \quad \eta(x) = 0 \\ \mu_k & \text{for} \quad \eta(x) = 1 \end{cases} \qquad \text{for all} \quad x \in G, \quad \eta \in \mathscr{X} \tag{2}$$

for $k = k(x, \eta)$ being the number of occupied neighbor sites of the site x in the configuration η. Throughout, we will consider exclusively the case in which

$$0 \leqslant \mu_i \leqslant \mu_{i-1} < \infty, \qquad i = 1, 2 \tag{3}$$

It is known that under the conditions (2) and (3) the operator $\mathscr{G}$ uniquely determines a strongly continuous Markov semigroup on $\mathscr{C}(\mathscr{X})$ which will be denoted by $\{S(t),\ t \geqslant 0\}$. The unique Markov process which corresponds to this semigroup will be called *an adsorption–desorption process* and designated by φ_t, $t \geqslant 0$; ADP will be the abbreviation for this process. $\mathscr{X}$ is the state space of an ADP. In this paper, we will be exclusively interested in the case when an ADP starts from the configuration $\varnothing$ (all sites empty). The probability distribution of φ_t, $t \geqslant 0$, will be designated by $\mathbb{P}\mathrm{r}$, the corresponding mathematical expectation operator will be designated by $\mathbb{E}$, so that for any $f \in \mathscr{C}(\mathscr{X})$, the following relationship holds:

$$(S(t)f)(\varnothing) = \mathbb{E}[f(\varphi_t)], \qquad \forall t \geqslant 0 \tag{4}$$

We will loosely call $\mathscr{G}$ *the generator* of φ_t, $t \geqslant 0$. The function $c(\cdot, \cdot)$ from (2) is called *the flip rate.* We will call λ *the adsorption rate* at an empty

site and μ_k *the desorption rate* from an occupied site surrounded by k occupied neighbors.

A particular case of ADP which is specified by the following condition imposed on the desorption rate,

$$\mu_0 = \mu > 0 \qquad \text{and} \qquad \mu_i = 0 \qquad \text{for all} \quad i \geqslant 1 \tag{5}$$

will be called the *sticking process* and denoted by ϕ_t, $t \geqslant 0$, throughout. The quantity μ will be called *the desorption rate of an isolated particle* in the sticking process. For this process, we say that a particle is *stuck* on G if it has at least one particle as its neighbor, since in this case, the particle is unable to leave G.

Remark. We set $\lambda = 1$ in (2) since multiplication of the flip rate function by a constant is equivalent to rescaling the time. Nevertheless, the symbol λ remains in our calculations since it helps to retain the dimension of the quantities.

The density function (also called *particle density function*), which is the subject of our research, is designated by $\rho(t)$, $t \geqslant 0$, and defined by

$$\rho(t) := \mathbb{E}[I_0(\varphi_t)], \qquad t \geqslant 0 \tag{6}$$

where $I_0 \in L(\mathscr{X})$ indicates the presence of a particle at the site $0 \in G$, i.e., $I_0(\eta) := \eta(0)$ for all $\eta \in \mathscr{X}$.

Regarding the shape of $\rho(t)$, $t \geqslant 0$, it is known that this function is concave when t is very small or very large. In fact, we recall that

$$\frac{d^2}{dt^2}\rho(0) = -\lambda(\lambda + \mu_0) < 0, \tag{7}$$

so that $\rho(t)$ is concave near the origin. [One may consult ref. 3, Corollary 1, for the proof of (7) or derive it directly from (15) by substituting $\varnothing$ for η and using (14).] We also recall that $\rho(t)$ is an increasing function of t since an ADP is an attractive spin system and the function I_0 is monotone on $\mathscr{X}$ [see Theorem 2.3(a) in ref. 10, Chapter III]. Since $\rho(t) \leqslant 1$, $\forall t$, one concludes that this function contains concave portions when t is large.

Assertion (i) of the following theorem gives a sufficient condition for the density function of sticking process to possess a convex portion.

Theorem. Let G be an infinite one-dimensional lattice or a finite one-dimensional lattice with a periodic boundary which contains more than seven sites. Let ϕ_t, $t \geqslant 0$, be a sticking process on G with the adsorption rate at an empty site being equal to $\lambda = 1$ and the desorption rate from an isolated occupied site equal to $\mu > 0$. Suppose that $\phi_0 = \varnothing$. Then:

(i) There is $\bar{\mu} < \infty$ such that for all $\mu \geqslant \bar{\mu}$,

$$\frac{d^2}{dt^2} \rho\left(\frac{2 \ln \mu}{\mu}\right) > 0$$

(ii) There is $\mu^* < \infty$ such that for all $\mu \geqslant \mu^*$,

$$\frac{d^2}{dt^2} \rho\left(\frac{\ln \mu}{\mu}\right) < 0$$

We would like to remark that assertion (ii) comes as a side result in the course of the proof of (i). However, (i) and (ii) together give an estimate on the time coordinate of the first inflection point of the density function, provided this function contains only one convex part. The latter fact is not proven in this paper. At the current stage of our knowledge we rely on our computer simulation results, which show that the density function of the sticking process is either concave or consists of three parts, the first and the last being concave and the intermediate one convex.

The usual approach based on the Trotter–Kurtz approximation theorem (Theorem 2.12 in ref. 10, Chapter I) allows one to derive from the theorem stated above that a convex part appears in the density function of an ADP if μ_0 is large and μ_k, $k \geqslant 1$, are small enough. We demonstrate this approach in the proof of the following corollary. The ADPs to which this corollary applies are reversible with respect to their invariant measures.

The set of reversible ADPs can be easily characterized. In fact, observe that if for some k, $\mu_k = 0$, then on account of (3), the configuration $\mathbb{1}$ (all sites occupied) is a trap. Therefore, if an ADP is reversible, then its flip rate is strictly positive. Change now 0 to -1 for designating an empty site in the definition of the ADP. The obtained process will then be a stochastic Ising model due to Theorem 2.13 in Chapter IV of ref. 10. Since the flip rate of an ADP is translation invariant and symmetric and depends on the nearest neighbors, then the potential to which the obtained stochastic Ising model relates should also possess these properties. Denote this potential by J_1, J_2 and express it in the usual way: $J_1 := \beta H$, $J_2 = \beta$. By definition, there are infinitely many stochastic Ising models relative to a given potential. A particular feature of the one that is obtained from an ADP is that the flip rate from -1 to $+1$ equals 1. The condition of detailed balance then gives that the flip rate from $+1$ to -1 at a site which is surrounded by k pluses equals

$$\mu_k = \exp\{4J_2 - 2J_1\} \exp\{-4J_2 k\}, \qquad k = 0, 1, 2 \tag{8}$$

The condition (8) is necessary and sufficient for an ADP to be reversible. Notice that (3) and (8) imply that $\beta \geqslant 0$.

Corollary. Let C be a positive constant greater than $\ln \bar{\mu}$. Assume that the value of a real number H depends on a positive real β through the relationship

$$2\beta(2-H)=C \tag{9}$$

Let G be a torus in $\mathbb{Z}^1$. Denote by $\varphi(t;\beta)$, $t\geqslant 0$, the ADP on G whose desorption rate has the form (8), where $J_1:=\beta H$, $J_2:=\beta>0$. Then there is a $\bar{\beta}<\infty$ such that for all $\beta\geqslant\bar{\beta}$, the density function of the process $\varphi(t;\beta)$, $t\geqslant 0$, possesses a convex part over some time interval. The value of $\bar{\beta}$ may depend on C and the size of G.

The following lemma will be used in the proof of the theorem. It gives the exact expression of the second derivative of the density function of the sticking process. The proof of the lemma itself is completely technical.

Lemma. Suppose the assumptions of the theorem above hold; then

$$\frac{d^2}{dt^2}\rho(t)=(\mu^2+3\lambda\mu)\,\mathbb{P}\mathrm{r}\{\phi_t\in\mathscr{X}_{\circ\bullet\circ}\}-(\mu\lambda+\lambda^2)\,\mathbb{P}\mathrm{r}\{\phi_t\in\mathscr{X}_{\circ\circ\circ}\}$$
$$-\lambda^2(\mathbb{P}\mathrm{r}\{\phi_t\in\mathscr{X}_{\circ\circ\bullet}\}+\mathbb{P}\mathrm{r}\{\phi_t\in\mathscr{X}_{\bullet\circ\circ}\}+\mathbb{P}\mathrm{r}\{\phi_t\in\mathscr{X}_{\bullet\circ\bullet}\}),\quad t\geqslant 0 \tag{10}$$

where

$$\mathscr{X}_{\circ\circ\circ}:=\{\eta\in\mathscr{X}:\eta(-1)=\eta(0)=\eta(1)=0\}$$
$$\mathscr{X}_{\circ\bullet\circ}:=\{\eta\in\mathscr{X}:\eta(-1)=1-\eta(0)=\eta(1)=0\}$$
$$\mathscr{X}_{\circ\circ\bullet}:=\{\eta\in\mathscr{X}:\eta(-1)=\eta(0)=1-\eta(1)=0\}$$
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$$\mathscr{X}_{\bullet\circ\bullet}:=\{\eta\in\mathscr{X}:1-\eta(-1)=\eta(0)=1-\eta(1)=0\}$$

Let us demonstrate roughly the idea and the method of the proof of the theorem. Consider a birth-and-death process which starts from $\varnothing$ and whose rates of birth and death are $\lambda=1$ and μ, respectively. This process will be denoted by ω_t, $t\geqslant 0$, throughout. For this process

$$p_t:=\mathbb{P}\mathrm{r}\{I_x(\omega_t)=1\}=\frac{\lambda}{\lambda+\mu}\{1-\exp[-(\lambda+\mu)t]\},\qquad t\geqslant 0 \tag{11}$$

for all $x\in G$, where $I_x\in L(\mathscr{X})$ is defined by $I_x(\eta):=\eta(x)$, $\eta\in\mathscr{X}$. [(11) is the solution for $p_t'=\lambda(1-p_t)-\mu p_t$ with the initial condition $p_0=0$.] Since

particles do not interact in ω_t, $t \geqslant 0$, the right-hand side of (10) acquires the following form, after the substitution of ω for ϕ:

$$(\mu^2 + 3\lambda\mu - 2\lambda^2)\, p_t^2(1-p_t) - (\mu\lambda + \lambda^2)\, p_t^3 - \lambda^2 p_t(1-p_t)^2 \qquad (12)$$

Now we take $t = t(\mu) = (c \ln \mu)/(\lambda + \mu)$ for some positive constant c and substitute $p_{t(\mu)}$ from (11) in (12). Elementary calculations show that the obtained expression approaches a positive value as $\mu \to \infty$ when c is not less than 1, while it is negative for all values of μ if c is sufficiently small. Consider now the sticking process ϕ_t, $t \geqslant 0$, whose desorption rate of an isolated particle equals μ. For this process, we observe that the number of the particles which have visited a lattice site before time $t(\mu)$ and the mean lifetime of a particle which equals $1/\mu$ are decreasing when $\mu \to \infty$ (by the mean lifetime we mean the mean time which a particle has spent on G before the desorption on the condition that it has not stuck on G). Thus, we conclude that the probability for particles to stick before time $t(\mu)$ in this sticking process is also decreasing in μ. This suggests that the distributions of $\phi_{t(\mu)}$ and $\omega_{t(\mu)}$ are close one to another for large values of μ. Therefore, the conclusion is that the difference between the values of (10) and (12) at $t(\mu)$ goes to zero when $\mu \to \infty$ and one expects that (10) is positive at time $t(\mu)$ for an appropriately chosen c. The birth-and-death process ω_t, $t \geqslant 0$, not only gives a correct choice for the function $t(\mu)$, but it is also essentially exploited in the proof of the theorem for estimating the probabilities involved in (10).

Let us give two more remarks regarding the existence of an inflection point in the density function of the sticking process.

First, we recall (see ref. 3 for the proof) that the density function of an ADP on an arbitrary lattice G is concave for all $t \geqslant 0$ provided

$$\max_{k=1,\ldots,s} (\mu_{k-1} - \mu_k) \leqslant s^{-1}(\lambda + \mu_s) \qquad (13)$$

where s is the number of neighbors of each site of the lattice G. For a sticking process on a one-dimensional lattice, $s = 2$ and the above inequality says $\mu \leqslant \lambda/2$, which explains why an inflection point cannot appear if μ is small.

Second, (11) suggests that the larger is the value of μ, the faster does the birth-and-death process reach its equilibrium state. Expressing p_∞ from (11), one easily checks that (12) is positive for the equilibrium state. Therefore, the value of t at which (12) becomes positive decreases when μ increases. Now, if one believes that ω and ϕ behave in a similar way when time is small and μ is large, then the above reasoning explains why the time coordinate of the first inflection point in the density function of the sticking process moves toward zero when μ increases.

3. PROOFS

Proof of Lemma. Applying the Hille–Yosida theorem (ref. 10, Theorem 2.9, Chapter I) twice to the cylinder function I_0, we get

$$\frac{d^2}{dt^2} S(t) I_0 = S(t)(\mathscr{G}^2 I_0), \qquad t \geqslant 0 \tag{14}$$

By (1),

$$\begin{aligned}(\mathscr{G}^2 I_0)(\eta) &= \sum_{x \in G} c(x, \eta)[\mathscr{G} I_0(\eta_x) - \mathscr{G} I_0(\eta)] \\ &= \sum_{x \in G} \sum_{y \in G} \{c(x, \eta)\, c(y, \eta_x)[I_0(\eta_{xy}) - I_0(\eta_x)] \\ &\quad - c(x, \eta)\, c(y, \eta)[I_0(\eta_y) - I_0(\eta)]\}\end{aligned}$$

where the symbol η_{uv} denotes the configuration η after it has been successively flipped at the sites $u, v \in G$, which need not be distinct. Observe that for the expressions surrounded by the square brackets to be different from 0, it is necessary that $y = 0$. Thus, the y summation reduces to $y = 0$. Next, we note that for each x such that $x \notin \{-1, 0, 1\}$, it holds that $c(x, \eta)\, c(0, \eta) = c(x, \eta)\, c(0, \eta_x)$ and $[I_0(\eta_{x0}) - I_0(\eta_x)] = [I_0(\eta_0) - I_0(\eta)]$. Consequently, for such x, the expression in the curly brackets is equal to zero. Therefore,

$$\begin{aligned}(\mathscr{G}^2 I_0)(\eta) = \sum_{x \in \{-1,0,1\}} & c(x, \eta)\{c(0, \eta_x)[I_0(\eta_{x0}) - I_0(\eta_x)] \\ & - c(0, \eta)[I_0(\eta_0) - I_0(\eta)]\}\end{aligned} \tag{15}$$

Let us divide $\mathscr{X}$ into 32 subsets by defining that two configurations belong to the same subset iff they coincide on the sites -2, -1, 0, 1, 2. Denote these subsets by $\mathscr{X}_1, \ldots, \mathscr{X}_{32}$. Since $c(z, \zeta)$ is completely characterized by the values of ζ on the neighbors of z, we derive from (15) that $\mathscr{G}^2 I_0(\eta)$ depends exclusively on $\eta(k)$ for $k \in [-2; 2]$, consequently, $\mathscr{G}^2 I_0$ equals a constant c_k on each $\mathscr{X}_k$, $k = 1, \ldots, 32$. After calculating the constants c_k, $k = 1, \ldots, 32$, from (15), one finds the following expression for $\mathscr{G}^2 I_0(\eta)$:

$$\begin{aligned}(\mathscr{G}^2 I_0)(\eta) = {} & (\mu^2 + 3\lambda\mu)\, I_{\mathscr{X}_{\circ\circ\circ}}(\eta) - (\mu\lambda + \lambda^2)\, I_{\mathscr{X}_{\circ\circ\circ}}(\eta) \\ & - \lambda^2[I_{\mathscr{X}_{\circ\circ\bullet}}(\eta) + I_{\mathscr{X}_{\circ\bullet\circ}}(\eta) + I_{\mathscr{X}_{\bullet\circ\circ}}(\eta)]\end{aligned} \tag{16}$$

where I_C is the indicator function of $C \subset \mathscr{X}$. Now, (10) follows from (16) due to (4), (6), and (14). This completes the proof. ∎

Proof of Theorem. We start the proof with an alternative construction of the sticking process ϕ_t, $t \geqslant 0$. This construction uses the concepts of graphical representation for interacting particle systems.

Let the sites of the lattice under consideration be drawn on a line of real numbers $\mathbb{R}$. At each site, we raise a time axis which is perpendicular to $\mathbb{R}$ and their intersection point corresponds to time $t = 0$. To each site, we arrange two independent Poisson point processes (PPP) which are also independent of the processes at the other sites. Their intensities are λ and μ, respectively (recall that $\lambda = 1$ due to the remark in Section 2). On each time axis, the first point of the first PPP is marked β (for birth or, equivalently, adsorption); the first point of the second PPP following the marked point is marked δ (for death or, equivalently, desorption); then the first point of the first PPP following this δ point is marked β, etc. Finally, the segments of the axis between the successive β's and δ's are painted black.

The obtained space-time diagram represents a realization of a birth-and-death process whose birth and death rates are equal to λ and μ, respectively, and which starts on an entirely empty lattice. A black segment means that the corresponding site is occupied by a particle; the particle's adsorption time is the beginning of the segment, and the desorption time is the end. The set of all space-time diagrams of the birth-and-death process is denoted by Ω. The measure on the distribution of β and δ points on each time axis is defined naturally by the considered Poisson processes. The set Ω is then endowed with the product measure.

Each diagram may be uniquely modified to become a realization of the sticking process with the parameters λ and μ. The modification rule is as follows. At each site of the lattice, we kill a particle at its desorption time if there are no particles at the neighboring sites; otherwise, the particle stays at the site forever and all the following β and δ points at this site are discarded. Let Φ denote the space of modified diagrams with the measure induced from the measure defined on Ω. There is a difficulty that arises in this algorithm, namely, there are ω's such that in order to decide whether to kill a particle at time t, we need to know the history of the whole lattice before t. This may cause a problem if the lattice is infinite. We will overcome this difficulty with the help of the sets $\Lambda_{-n,m}$ introduced below. Actually, the measure of these ω's is zero.

Let $\omega \in \Omega$; by ω_t we denote the section of this diagram at time t, and $\omega(k)$ stands for the section at the site $k \in G$; the symbols ϕ_t and $\phi(k)$ have the corresponding meaning for $\phi \in \Phi$.

Remark. Recall that according to the definitions given in Section 2, the symbol $\mathbb{P}\mathrm{r}$ designates the probability distribution of the process ϕ_t,

$t \geqslant 0$. No confusion will arise if we use the same symbol $\mathbb{P}\mathrm{r}$ to designate the probability distribution of the process ω_t, $t \geqslant 0$, from which ϕ_t, $t \geqslant 0$, is constructed.

We will need the following auxiliary functions:

$$\beta_t(\omega(k)) := \text{the number of } \beta\text{-points in } \omega(k) \text{ up to time } t$$

$$\beta_t(\phi(k)) := \text{the number of } \beta\text{-points in } \phi(k) \text{ up to time } t$$

From here on, let T be a fixed time whose value will be specified later.

For $n, m \in Z^+$, denote by $\Lambda_{-n,m} = \Lambda_{-n,m}(T)$ the set of all $\phi \in \Phi$ such that:

(i) $\beta_T(\phi(-n)) = \beta_T(\phi(m)) = 0$.

(ii) $\beta_T(\phi(k)) \geqslant 1$ for all $k \in (-n; m) \setminus \{0\}$.

Remark. Assume $Y \subset \Phi$ is defined by giving the states of the sites $-n, -n+1, \ldots, m$ at time T and the number of particles which have visited each of these sites by time T. We remark that if the inclusion $Y \subset \Lambda_{-n,m}$ holds, then $\mathbb{P}\mathrm{r}\{Y\}$ is easily evaluated. In fact, denote by $W \subset \Omega$ the set of all $\omega \in \Omega$ for which the corresponding modified realization ϕ belongs to Y. Then, to determine whether an $\omega \in \Omega$ belongs to W, one needs only to know $\{\omega_s(k), -n \leqslant k \leqslant m, 0 \leqslant s \leqslant T\}$ because everything that "happens" to ω outside the interval $[-n, m]$ can be neglected since the birth-free sites $-n$ and m protect the interior of the interval from influence from outside. Consequently, $\mathbb{P}\mathrm{r}\{W\}$ can be expressed as a multiple integral. In what follows, T is small; consequently, the integral's value is easily evaluated. Since $\mathbb{P}\mathrm{r}\{W\}$ equals $\mathbb{P}\mathrm{r}\{Y\}$, this solves the problem of evaluating the latter. Below, we demonstrate this calculation for $Y = B_7$ from (18).

We also remark that (ii) provides that the sets $\Lambda_{-n,m}$, $n, m \in Z^+$, are mutually nonintersecting.

In the following exposition, the symbol k_j^i is used to retain the history of a site k until time T in the sticking process. More precisely, the number k stands for a site of the considered lattice; if the value of the subscript is j, it means that exactly j particles have adsorbed at this site until time T; if the site is empty (occupied) at time T, we assign the value 0 (respectively, 1) to the superscript. We use an asterisk for the superscript if we allow the site to be either empty or occupied (at time T); and use an asterisk for the subscript if the number of particles which have adsorbed before time T is not important to us. Once more, notice that the symbol k_j^i refers to the sticking process.

For example, the set B_7 defined in (18) below is interpreted as the set of all realizations of the sticking process for which the sites -2 and 1 have had no adsorptions before T, the site 0 has been visited by two particles

and the second one occupies this site at time T, and the site -1 has been visited by one particle which has left it before T. Notice that by specifying the states of the sites at time T, we in particular state that the particles at the sites -1 and 0 have not stuck before T. Notice also that, by the construction, $B_7 \subset \Lambda_{-2,1}$. Consequently, B_7 may be expressed as a subset of Ω in the way presented in Fig. 1. According to this presentation, its probability is given by the following multiple integral:

$$\begin{aligned}\mathbb{P}\mathrm{r}\{B_7\} = &\int_0^T \lambda e^{-\lambda x}\,dx \int_0^{T-x} \mu e^{-\mu y}\,dy \int_0^{T-x-y} \lambda e^{-\lambda u}\,du \int_{T-x-y-u}^{\infty} \mu e^{-\mu z}\,dz \\ &\times \left\{ \int_{x+y}^{x+y+u} \lambda e^{-\lambda w}\,dw \int_0^{x+y+u-w} \mu e^{-\mu v}\,dv \int_{T-w-v}^{\infty} \lambda e^{-\lambda q}\,dq \right. \\ &\left. + \int_0^{x} \lambda e^{-\lambda w}\,dw \int_0^{x-w} \mu e^{-\mu v}\,dv \int_{T-w-v}^{\infty} \lambda e^{-\lambda q}\,dq \right\} \qquad (17)\end{aligned}$$

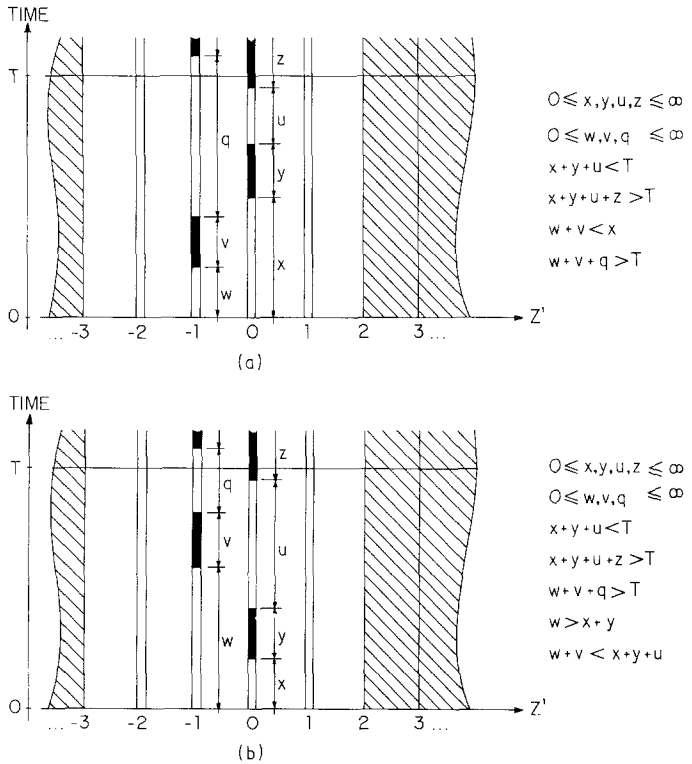

Fig. 1. A realization ϕ belongs to B_7 iff its adsorption and desorption events at the sites -2, -1, 0, and 1 occurr as shown in (a) or (b) for appropriate values of x, y, z, u, w, v, and q and independently of everything that happens at the other sites of the lattice.

We have prepared everything we need to proceed to the proof of the theorem in the way outlined in the previous section after formulation of the lemma.

We define $A_i = A_i(T)$, $B_i = B_i(T) \subset \Phi$, $i = 1,..., 12$, and $C_i = C_i(T)$, $D_i = D_i(T) \subset \Phi$, $i = 1,..., 4$, in the following manner:

$$
\begin{aligned}
A_1 &:= \{-1_0^0, 0_0^0, 1_0^0\}, & B_1 &:= \{-1_0^0, 0_1^1, 1_0^0\} & &\subset \Lambda_{-1,1}\\
A_2 &:= \{-1_0^0, 0_1^0, 1_0^0\}, & B_2 &:= \{-1_0^0, 0_2^1, 1_0^0\} & &\subset \Lambda_{-1,1}\\
A_3 &:= \{-1_0^0, 0_0^0, 1_1^0, 2_0^0\}, & B_3 &:= \{-1_0^0, 0_1^1, 1_1^0, 2_0^0\} & &\subset \Lambda_{-1,2}\\
A_4 &:= \{-2_0^0, -1_1^0, 0_0^0, 1_0^0\}, & B_4 &:= \{-2_0^0, -1_1^0, 0_1^1, 1_0^0\} & &\subset \Lambda_{-2,1}\\
A_5 &:= \{-1_0^0, 0_2^0, 1_0^0\}, & B_5 &:= \{-1_0^0, 0_3^1, 1_0^0\} & &\subset \Lambda_{-1,1}\\
A_6 &:= \{-1_0^0, 0_1^0, 1_1^0, 2_0^0\}, & B_6 &:= \{-1_0^0, 0_1^1, 1_1^0, 2_0^0\} & &\subset \Lambda_{-1,2}\\
A_7 &:= \{-2_0^0, -1_1^0, 0_1^0, 1_0^0\}, & B_7 &:= \{-2_0^0, -1_1^0, 0_2^1, 1_0^0\} & &\subset \Lambda_{-2,1}\\
A_8 &:= \{-1_0^0, 0_0^0, 1_2^0, 2_0^0\}, & B_8 &:= \{-1_0^0, 0_1^1, 1_2^0, 2_0^0\} & &\subset \Lambda_{-1,2}\\
A_9 &:= \{-2_0^0, -1_2^0, 0_0^0, 1_0^0\}, & B_9 &:= \{-2_0^0, -1_2^0, 0_1^1, 1_0^0\} & &\subset \Lambda_{-2,1}\\
A_{10} &:= \{-1_0^0, 0_0^0, 1_1^0, 2_1^*, 3_0^0\}, & B_{10} &:= \{-1_0^0, 0_1^1, 1_1^0, 2_1^*, 3_0^0\} & &\subset \Lambda_{-1,3}\\
A_{11} &:= \{-3_0^0, -2_1^*, -1_1^0, 0_0^0, 1_0^0\}, & B_{11} &:= \{-3_0^0, -2_1^*, -1_1^0, 0_1^1, 1_0^0\} & &\subset \Lambda_{-3,1}\\
A_{12} &:= \{-2_0^0, -1_1^0, 0_0^0, 1_1^0, 2_0^0\}, & B_{12} &:= \{-2_0^0, -1_1^0, 0_1^1, 1_1^0, 2_0^0\} & &\subset \Lambda_{-2,2}
\end{aligned}
\tag{18}
$$

and

$$
\begin{aligned}
C_1 &:= \{-1_1^1, 0_0^0, 1_0^0\}, & D_1 &:= \{-1_0^0, 0_0^0, 1_1^1\}\\
C_2 &:= \{-1_2^1, 0_0^0, 1_0^0\}, & D_2 &:= \{-1_0^0, 0_0^0, 1_2^1\}\\
C_3 &:= \{-1_1^1, 0_1^0, 1_0^0\}, & D_3 &:= \varnothing\\
C_4 &:= \varnothing, & D_4 &:= \{-1_0^0, 0_1^0, 1_1^1\}
\end{aligned}
\tag{19}
$$

Due to the definitions (18) and (19), it holds that

$$
\begin{gathered}
A_i \cap A_j = \varnothing, \qquad B_i \cap B_j = \varnothing, \qquad C_i \cap C_j = \varnothing\\
D_i \cap D_j = \varnothing, \qquad i \neq j
\end{gathered}
\tag{20}
$$

and also the following implications are valid:

$$
\begin{aligned}
&\phi \in \bigcup_{i=1}^{12} A_i \Rightarrow \phi_T \in \mathcal{X}_{\circ\circ\circ}, \qquad \phi \in \bigcup_{i=1}^{12} B_i \Rightarrow \phi_T \in \mathcal{X}_{\bullet\circ\circ}\\
&\phi \in \bigcup_{i=1}^{4} C_i \Rightarrow \phi_T \in \mathcal{X}_{\circ\bullet\circ}, \qquad \phi \in \bigcup_{i=1}^{4} D_i \Rightarrow \phi_T \in \mathcal{X}_{\circ\circ\bullet}
\end{aligned}
\tag{21}
$$

The choice of the events A_i and B_i presented in (18) is subjected to the needs of the proof of (i). However, for the sake of simplicity of the exposition, we first derive the assertion (ii). To do it, we need the probabilities of A_i, B_i, C_i, D_i, $i=1,\ldots,4$. Using the approach demonstrated above for $\Pr\{B_7\}$ [see (17) and the preceding argument], we obtain the following results:

$$\begin{aligned}
&\mathbb{P}\mathrm{r}\{A_1\} = e^{-3\lambda T} \\
&\mathbb{P}\mathrm{r}\{B_1\} = \mathbb{P}\mathrm{r}\{C_1\} = \mathbb{P}\mathrm{r}\{D_1\} = \frac{e^{-3\lambda T}\lambda}{\mu-\lambda}(1-e^{-(\mu-\lambda)T}) \\
&\mathbb{P}\mathrm{r}\{A_2\} = e^{\lambda T}\,\mathbb{P}\mathrm{r}\{A_3\} = e^{\lambda T}\,\mathbb{P}\mathrm{r}\{A_4\} = \frac{e^{-3\lambda T}\lambda\mu}{\mu-\lambda}\left(T - \frac{1-e^{-(\mu-\lambda)T}}{\mu-\lambda}\right) \\
&\mathbb{P}\mathrm{r}\{B_2\} = e^{\lambda T}\,\mathbb{P}\mathrm{r}\{B_3\} = e^{\lambda T}\,\mathbb{P}\mathrm{r}\{B_4\} = \mathbb{P}\mathrm{r}\{C_2\} = \mathbb{P}\mathrm{r}\{C_3\} \\
&\quad = \mathbb{P}\mathrm{r}\{D_2\} = \mathbb{P}\mathrm{r}\{D_4\} = \frac{e^{-3\lambda T}\lambda^2\mu}{(\mu-\lambda)^2}\left(T(1-e^{-(\mu-\lambda)T}) - \frac{2(1-e^{-(\mu-\lambda)T})}{\mu-\lambda}\right)
\end{aligned} \tag{22}$$

Taking $T=\ln\mu/(\mu-\lambda)$ and $\lambda=1$ in the above expressions and expanding the exponent and the function $(\mu-\lambda)^{-1}$ in Taylor series about the origin, we get

$$\begin{aligned}
&\sum_{i=1}^{4}\{(\mu^2+3\lambda\mu)\,\mathbb{P}\mathrm{r}\{B_i\} - (\lambda\mu+\lambda^2)\,\mathbb{P}\mathrm{r}\{A_i\} - \lambda^2(\mathbb{P}\mathrm{r}\{C_i\} + \mathbb{P}\mathrm{r}\{D_i\})\} \\
&\quad = -\mu + 11\ln\mu + O(1)
\end{aligned} \tag{23}$$

where the sign O means the asymptotics with respect to $\mu\to\infty$.

Now notice that

$$\phi_T \in \mathscr{X}_{\circ\bullet\circ} \text{ and } \phi \notin \bigcup_{i=1}^{4} B_i \;\Rightarrow\; \sum_{k=-2}^{2} \beta_T(\phi(k)) \geqslant 3 \tag{24}$$

This implication follows from the definition (18). In particular, it becomes clear, if one recalls that the sets $\Lambda_{-n,m}$, $n, m\in\mathbb{Z}^+$, are nonintersecting and each B_i belongs to one of these sets as indicated in the first four lines of (18). Consequently,

$$\begin{aligned}
\mathbb{P}\mathrm{r}\left\{\phi\colon \phi_T\in\mathscr{X}_{\circ\bullet\circ},\ \phi\notin\bigcup_{i=1}^{4}B_i\right\} &\leqslant \mathbb{P}\mathrm{r}\left\{\omega\colon \sum_{k=-2}^{2}\beta_T(\omega(k))\geqslant 3\right\} \\
&= e^{-5\lambda T}\sum_{l=3}^{\infty}\frac{(5\lambda T)^l}{l!} = O(T^3) = O\left(\frac{\ln^3\mu}{\mu^3}\right)
\end{aligned} \tag{25}$$

Applying (23) and (25) to (10) of the lemma and using (21) and (20), we obtain that $d^2\rho(T)/dt^2 < -\mu + O(\ln \mu)$ for $T = (\ln \mu)/(\mu - \lambda)$ as $\mu \to \infty$, which demonstrates (ii) of the theorem.

Assertion (i) of the theorem was proven in the following way. First, for each A_i, B_i, $i = 5,..., 12$, we expressed its probability by a (17)-like integral using the approach demonstrated above for B_7. Then we calculated explicitly the value of this integral. Afterward, we substituted $(2 \ln \mu)/(\mu - \lambda)$ for T and expanded the obtained result in the form presented below. Notice, once more, that in the following formulas, T is just an abbreviation of $(2 \ln \mu)/(\mu - \lambda)$ and $\lambda = 1$ according to the remark from the previous section. We have

$$\mathbb{P}\mathrm{r}\{A_5\} = e^{\lambda T}\,\mathbb{P}\mathrm{r}\{A_8\} = e^{\lambda T}\,\mathbb{P}\mathrm{r}\{A_9\}$$
$$= \frac{\lambda^2\mu^2 e^{-3\lambda T}}{(\mu-\lambda)^2}\left[\frac{1}{2}T^2 - \frac{2T}{\mu-\lambda} + \frac{3}{(\mu-\lambda)^2} + o\left(\frac{1}{\mu^2}\right)\right]$$

$$\mathbb{P}\mathrm{r}\{B_5\} = e^{\lambda T}\,\mathbb{P}\mathrm{r}\{B_8\} = e^{\lambda T}\,\mathbb{P}\mathrm{r}\{B_9\}$$
$$= \frac{\lambda^3\mu^2 e^{-3\lambda T}}{(\mu-\lambda)^3}\left[\frac{1}{2}T^2 - \frac{3T}{\mu-\lambda} + \frac{6}{(\mu-\lambda)^2} + o\left(\frac{1}{\mu^2}\right)\right]$$

$$\mathbb{P}\mathrm{r}\{A_6\} = \mathbb{P}\mathrm{r}\{A_7\} = \frac{\lambda^2\mu^2 e^{-4\lambda T}}{(\mu-\lambda)^2}\left[T^2 - \frac{4T}{\mu-\lambda} + \frac{6}{(\mu-\lambda)^2} + o\left(\frac{1}{\mu^2}\right)\right]$$

$$\mathbb{P}\mathrm{r}\{B_6\} = \mathbb{P}\mathrm{r}\{B_7\} = \frac{\lambda^3\mu^2 e^{-4\lambda T}}{(\mu-\lambda)^3}\left[T^2 - \frac{6T}{\mu-\lambda} + \frac{13}{(\mu-\lambda)^2} + o\left(\frac{1}{\mu^2}\right)\right]$$

$$\mathbb{P}\mathrm{r}\{A_{10}\} = \mathbb{P}\mathrm{r}\{A_{11}\}$$
$$= \frac{\lambda^2\mu^2 e^{-5\lambda T}}{(\mu-\lambda)^2}\left[T^2 - \left(\frac{4}{\mu-\lambda} - \frac{1}{\mu}\right)T + \left(\frac{6}{(\mu-\lambda)^2} - \frac{2}{\mu(\mu-\lambda)}\right) + o\left(\frac{1}{\mu^2}\right)\right]$$

$$\mathbb{P}\mathrm{r}\{B_{10}\} = \mathbb{P}\mathrm{r}\{B_{11}\}$$
$$= \frac{\lambda^3\mu^2 e^{-5\lambda T}}{(\mu-\lambda)^3}\left[T^2 - \left(\frac{5}{\mu-\lambda} - \frac{1}{\mu}\right)T + \left(\frac{8.5}{(\mu-\lambda)^2} - \frac{2.5}{\mu(\mu-\lambda)}\right) + o\left(\frac{1}{\mu^2}\right)\right]$$

$$\mathbb{P}\mathrm{r}\{A_{12}\} = \frac{\lambda^2\mu^2 e^{-5\lambda T}}{(\mu-\lambda)^2}\left[T^2 - \frac{2T}{\mu-\lambda} + \frac{1}{(\mu-\lambda)^2} + o\left(\frac{1}{\mu^2}\right)\right]$$

$$\mathbb{P}\mathrm{r}\{B_{12}\} = \frac{\lambda^3\mu^2 e^{-5\lambda T}}{(\mu-\lambda)^3}\left[T^2 - \frac{4T}{\mu-\lambda} + \frac{5}{(\mu-\lambda)^2} + o\left(\frac{1}{\mu^2}\right)\right]$$

It is easy to see from the above presentation that

$$\begin{aligned}\Delta_i &:= (\mu^2 + 3\lambda\mu)\,\Pr\{B_i\} - (\lambda\mu + \lambda^2)\,\Pr\{A_i\} \\ &= (\mu^2 + 3\lambda\mu)\,\Pr\{B_i\} - \frac{\lambda}{(\mu-\lambda)}(\mu^2 - \lambda^2)\,\Pr\{A_i\} \\ &= \frac{\lambda^3\mu^2 e^{-\gamma\lambda T}}{(\mu-\lambda)^3}\left[-\frac{K_i T\mu^2}{\mu-\lambda} + \frac{L_i\mu^2}{(\mu-\lambda)^2} + o(1)\right], \qquad i = 5,\ldots, 12 \end{aligned} \tag{26}$$

where γ is either 3, 4, or 5 and K_i, L_i are positive constants. We note that the form of the leading term in the expansion of Δ_i given by the rightmost expression of (26) is determined by the coefficient of the second term in the expansions for the probabilities of A_i and B_i, $i = 5,\ldots, 12$. This is due to the fact that the ratio between the coefficients of T^2 in $\Pr\{A_i\}$ and $\Pr\{B_i\}$ is $(\mu-\lambda)/\lambda$ for all $i = 5,\ldots, 12$. Actually, we intended to achieve this effect by the construction (18).

Next, using the Taylor expansion for $e^{-\gamma\lambda T}$ and $(\mu-\lambda)^{-1}$, we obtain

$$\sum_{i=5}^{12} [(\mu^2 + 3\lambda\mu)\,\Pr\{B_i\} - (\lambda\mu + \lambda^2)\,\Pr\{A_i\}] = -11T + 31/\mu + o(1/\mu)$$

On the other hand, under $T = (2\ln\mu)/(\mu-\lambda)$ and $\lambda = 1$, the relationships (22) yield

$$\begin{aligned}&\sum_{i=1}^{4} \{(\mu^2 + 3\lambda\mu)\,\Pr\{B_i\} - (\lambda\mu + \lambda^2)\,\Pr\{A_i\} - \lambda^2(\Pr\{C_i\} + \Pr\{D_i\})\} \\ &\quad = 11T - 14/\mu + o(1/\mu)\end{aligned}$$

So, our conclusion is that

$$\begin{aligned}&\sum_{i=1}^{12} \{(\mu^2 + 3\lambda\mu)\,\Pr\{B_i\} - (\lambda\mu + \lambda^2)\,\Pr\{A_i\}\} - \sum_{i=1}^{4} \{\lambda^2(\Pr\{C_i\} + \Pr\{D_i\})\} \\ &\quad = 17/\mu + o(1/\mu)\end{aligned} \tag{27}$$

The last stage of the proof is to show that the difference between the left-hand side of (27) and the right-hand side of (10) is $o(1/\mu)$.

First, notice that if $\phi_T \in \mathscr{X}_{\infty\infty}$ and $\phi \notin \bigcup_{i=1}^{12} A_i$, then $\sum_{k=-3}^{3} \beta_T(\phi(k)) \geqslant 3$. This implication is obtained exactly as (24), and, consequently, in the way analogous to that used to derive (25) from (24), we get that

$$\Pr\left\{\phi: \phi_T \in \mathscr{X}_{\infty\infty} \text{ and } \phi \notin \bigcup_{i=1}^{12} A_i\right\} \leqslant e^{-7\lambda T} \sum_{k=3}^{\infty} \frac{(7\lambda T)^k}{k!} = O(T^3) \tag{28}$$

Next, we are going to estimate the difference between $\mathbb{P}\mathrm{r}\{\phi_T \in \mathscr{X}_{\circ\circ\bullet}\}$ and $\mathbb{P}\mathrm{r}\{\bigcup_{i=1}^{4} D_i\}$. To do this we have to distinguish between two cases, one when a particle that occupies the site 1 at time T is isolated at this time, and the other when it belongs to a cluster of particles which extends to the right of the site 1 at time T. Formally speaking, $\phi_T(2)$ is 0 for the first case and 1 for the second one. Regarding the first case, we notice that if $\phi_T \in \mathscr{X}_{\circ\circ\bullet}$, $\phi_T(2)=0$, and $\phi \notin \bigcup_{i=1}^{4} D_i$, then either $\phi \in \{-1_1^0, 0_0^0, 1_1^1, 2_*^0\}$ or $\sum_{k=-1}^{1} \beta_T(\phi(k)) \geqslant 3$. The probabilities of these two alternatives are estimated as follows:

$$\begin{aligned}
&\mathbb{P}\mathrm{r}\{\phi: \phi \in \{-1_1^0, 0_0^0, 1_1^1, 2_*^0\}\} \\
&\quad \leqslant \mathbb{P}\mathrm{r}\{\omega: \beta_T(\omega(-1))=1\}\, \mathbb{P}\mathrm{r}\{\omega: \beta_T(\omega(1))=1, \omega_T(1)=1\} \\
&\quad = O(T/(\mu-\lambda))
\end{aligned}$$

and

$$\mathbb{P}\mathrm{r}\left\{\phi: \sum_{k=-1}^{1} \beta_T(\phi(k)) \geqslant 3\right\} \leqslant \mathbb{P}\mathrm{r}\left\{\omega: \sum_{k=-1}^{1} \beta_T(\omega(k)) \geqslant 3\right\} = O(T^3)$$

For the second case to be realized, at least one adsorption should occur at each of the sites 1 and 2. Discounting everything that happens outside of these sites, we obtain that the probability of this event is $O(T^2)$.

Summarizing the above reasoning, we get the following estimate:

$$\left|\mathbb{P}\mathrm{r}\{\phi: \phi_T \in \mathscr{X}_{\circ\circ\bullet}\} - \mathbb{P}\mathrm{r}\left\{\bigcup_{i=1}^{4} D_i\right\}\right| = O(T^2) \tag{29}$$

and, analogously,

$$\left|\mathbb{P}\mathrm{r}\{\phi: \phi_T \in \mathscr{X}_{\circ\circ\circ}\} - \mathbb{P}\mathrm{r}\left\{\bigcup_{i=1}^{4} C_i\right\}\right| = O(T^2) \tag{30}$$

Finally, a sufficiently good estimate of $\mathbb{P}\mathrm{r}\{\phi: \phi_T \in \mathscr{X}_{\bullet\circ\bullet}\}$ is provided by the following inequality:

$$\begin{aligned}
&\mathbb{P}\mathrm{r}\{\phi: \phi_T \in \mathscr{X}_{\bullet\circ\bullet}\} \\
&\quad \leqslant \mathbb{P}\mathrm{r}\{\omega: \beta_T(\omega(-1)) \geqslant 1 \text{ and } \beta_T(\omega(1)) \geqslant 1\} = O(T^2)
\end{aligned} \tag{31}$$

Now the relationships (21) and (20) and the estimates (28)–(31) determine that the difference between the right-hand side of (10) and the left-hand side of (27) is $o(1/\mu)$. Thus, by the lemma's assertion and Eq. (27), it holds that

$$\left(\frac{d^2}{dt^2}\right)\rho(T) \geqslant 17/\mu + o(1/\mu) \quad \text{for} \quad T = 2\ln\mu/(\mu-\lambda) \quad \text{when} \quad s \to \infty \tag{32}$$

which proves (i) of the theorem. Regarding the lattice size, notice that we have used in the definition (18) the fact that there are at least three sites on the left and three on the right of the site 0. This is reflected in the theorem's assumptions. ∎

Proof of Corollary. Let $S_\beta(t)$, $t \geqslant 0$, and $\mathscr{G}_\beta$ be, respectively, the semigroup and the generator of the process $\varphi(t;\beta)$, $t \geqslant 0$. Reasoning as in the proof of the lemma, it is easy to show that the function $\mathscr{G}_\beta^2 I_0$ is expressed by the right-hand side of (15) and, consequently, this function acquires a constant value on each $\mathscr{X}_k$, $k = 1,..., 32$. The subsets $\mathscr{X}_1,..., \mathscr{X}_{32}$ have been introduced in the proof of the lemma. Denote by $\mathscr{Y}_1,..., \mathscr{Y}_{16}$ those of them which are not contained in any one of the sets $\mathscr{X}_{\circ\circ\circ}$, $\mathscr{X}_{\circ\bullet\circ}$, $\mathscr{X}_{\bullet\circ\circ}$, $\mathscr{X}_{\circ\circ\bullet}$, $\mathscr{X}_{\bullet\circ\bullet}$. A straightforward calculation gives that

$$\begin{aligned}(\mathscr{G}_\beta^2 I_0)(\eta) = {} & (\mu^2 + 3\lambda\mu - 2\lambda\mu_1)\, I_{\mathscr{X}_{\bullet\circ\circ}}(\eta) - (\mu\lambda + \lambda^2)\, I_{\mathscr{X}_{\circ\circ\circ}}(\eta) \\ & - (\lambda^2 + \lambda\mu_1)[I_{\mathscr{X}_{\circ\circ\bullet}}(\eta) + I_{\mathscr{X}_{\bullet\circ\circ}}(\eta)] \\ & - (\lambda^2 + \lambda\mu_2)\, I_{\mathscr{X}_{\bullet\circ\bullet}}(\eta) + \sum_{k=1}^{16} a_k I_{\mathscr{Y}_k}(\eta) \end{aligned} \tag{33}$$

where

$$a_k = a_{k1}\lambda\mu_1 + a_{k2}\lambda\mu_2 + ak3\mu_1\mu_2, \qquad a_{ki} \in \mathbb{R}, \quad i = 1, 2, 3, \quad k = 1,..., 16 \tag{34}$$

Let now ϕ_t, $t \geqslant 0$, be the sticking process on G whose desorption rate of an isolated particle equals $\mu_0 = \exp\{2\beta(2-H)\}$. Denote by $S(t)$, $t \geqslant 0$, and $\mathscr{G}$, respectively, the semigroup and the generator of this process. By (9), (8), and the choice of C, $\mu_0 \geqslant \bar{\mu}$; thus, due to (i) of the theorem formulated in Section 2, the density function of this process possesses a convex part. Moreover, the inequality (32) from the proof of this theorem gives that

$$S(T)(\mathscr{G}^2 I_0)(\varnothing) > 17/\mu_0, \qquad \text{where} \quad T = (2\ln\mu_0)/(\mu_0 - 1) \tag{35}$$

Recall that $\mathscr{G}^2 I_0$ is given by (16); thus, comparing the latter with (33), we obtain that

$$(\mathscr{G}_\beta^2 I_0)(\eta) = (\mathscr{G}^2 I_0)(\eta) + g(\eta), \qquad \forall \eta \in \mathscr{X} \tag{36}$$

for a certain $g \in C(\mathscr{X})$ which satisfies, on account of (34), $\max_{\eta\in\mathscr{X}} |g(\eta)| \leqslant c^*\mu_1$ for an appropriate positive c^*. The latter inequality and (36) yield

$$|S_\beta(t)(\mathscr{G}_\beta^2 I_0)(\varnothing) - S_\beta(t)(\mathscr{G}^2 I_0)(\varnothing)| \leqslant c^*\mu_1, \qquad \forall t \geqslant 0 \tag{37}$$

Now observe that

$$\mu_i \to 0, \quad i = 1, 2, \quad \text{as} \quad \beta \to \infty \quad \text{while } \mu_0 \text{ does not depend on } \beta \tag{38}$$

Using the definition (1) and (38), it is easy to see that $\mathcal{G}_\beta f \to \mathcal{G} f$ as $\beta \to \infty$ for every cylinder function f. But then the Trotter–Kurtz approximation theorem (Theorem 2.12 in Chapter I of ref. 10) gives that

$$S_\beta(T)(\mathcal{G}^2 I_0) \to S(T)(\mathcal{G}^2 I_0) \qquad \text{as} \quad \beta \to \infty \tag{39}$$

Now, combining (35), (37), and (39) and using (38), we conclude that if β is greater than a certain finite $\bar{\beta}$, then $S_\beta(T)(\mathcal{G}_\beta^2 I_0)(\varnothing) > 0$. The expression in the left-hand side of the latter inequality equals $(d^2/dt^2)\, \mathbb{E}[I_0(\varphi(t;\beta))]\,|_{t=T}$; thus, the proof of the corollary is completed. Among the factors which determine the value of $\bar{\beta}$, there are the rate of convergence in (39) and the lower bound of $S(T)(\mathcal{G} I_0)(\varnothing)$; consequently, $\bar{\beta}$ may depend on the size of G and the choice of C (since $\mu_0 = \exp C$). ▮

4. CLOSING REMARKS

R1. In the case of an ADP, a sufficient condition for a spin system to be ergodic (ref. 10, Chapter III.0) on an arbitrary lattice G acquires the following form: $\max_{k=1,\ldots,s}(\mu_{k-1} - \mu_k) < s^{-1}(\lambda + \mu_s)$, where $s := \deg G$ is the number of neighbors of each site of the lattice G. With the strong inequality being replaced by the weak one, this is exactly (13), a sufficient condition for an ADP to possess a density function which is concave for all $t \geqslant 0$. Since a sticking process is ergodic, our result shows that there may be no deep connection between the ergodicity of an ADP and the concavity of its density function. However, the coincidence of their sufficient conditions is intriguing.

R2. A sticking process may have a nonconcave density function not only on one-dimensional lattices. This fact is substantiated by a computer simulation. Our method seems to work for higher dimensions. However, in these cases, the right-hand side of (10) would depend on more than five events and an attempt to evaluate their probabilities using our method will blow up the constructions (18) and (19). As has been mentioned, we intend to treat these cases with the assistance of a computer.

R3. Let φ_t, $t \geqslant 0$, be an adsorption–desorption process on an arbitrary lattice G which corresponds to the following choice of the desorption rate: $\mu_k := \Lambda(s-k)$, $k = 0, \ldots, \deg G$, for some positive Λ. Denote by $\mathbb{1} \in \mathcal{X}$ a fully occupied configuration defined by $\mathbb{1}(x) := 1$ for all $x \in G$. Then,

$\xi_t := \mathbb{1} - \varphi_t$, $t \geqslant 0$, coincides with a contact process that starts from the state "all individuals infected" and the rate of the infection's spread is equal to Λ. The density of the ADP is then the density of the healthy individuals of the corresponding contact process. Will it be a nonconcave function of time if Λ is large? Our method does not seem to work for the contact process.

R4. Observe that $\mathbb{Z}^3$ and a triangular planar lattice have the same degree, 6, but are not isomorphic; let us loosely say that they have different "geometries." It has been shown in ref. 4 that an ADP with the same flip rate will have different density functions on these lattices. Will the lattice geometry also affect an inflection point? An answer to this question may help us to infer the structure of the bonds between the interacting molecules.

ACKNOWLEDGMENTS

My interest in the adsorption–desorption process, to which the results of this paper relate, was stimulated by my Ph.D. advisor Boris L. Granovsky, to whom I am indebted. I also thank Bernard Ycart for fruitful discussions. The suggestions made by Daniel B. Henry and a referee helped to improve the style of this article. This work was supported by Fundacão de Ampara à Pesquisa do Estado de São Paulo, grant 91/3312-2. The research reported here was begun at the Technion-Israel Institute of Technology.

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