Adsorption of a binary mixture of monomers with nearest neighbour cooperative effects

2005 J. Phys. A: Math. Gen. 38 7051

(http://iopscience.iop.org/0305-4470/38/32/001)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS A: MATHEMATICAL AND GENERAL

J. Phys. A: Math. Gen. **38** (2005) 7051–7066 doi:10.1088/0305-4470/38/32/001

Adsorption of a binary mixture of monomers with nearest neighbour cooperative effects

A Prados and J J Brey

Física Teórica, Universidad de Sevilla, Apartado de Correos 1065, E-41080 Sevilla, Spain

E-mail: prados@us.es and brey@us.es

Received 4 May 2005, in final form 30 June 2005
Published 27 July 2005
Online at stacks.iop.org/JPhysA/38/7051

Abstract

A model for the adsorption of a binary mixture on a one-dimensional infinite lattice with nearest neighbour cooperative effects is considered. The particles of the two species are both monomers but differ in the repulsive interaction experienced by them when trying to adsorb. An exact expression for the coverage of the lattice is derived. In the jamming limit, it is a monotonic function of the ratio between the attempt frequencies of the two species, varying between the values corresponding to each of the two single species. This is in contrast with the results obtained in other models for the adsorption of particles of different sizes. The structure of the jamming state is also investigated.

PACS numbers: 02.50.Ey, 68.43.Mn, 05.50.+q

1. Introduction

The adsorption of particles on a solid substrate is a process occurring in many natural phenomena and that, consequently, has been extensively studied both experimentally and theoretically [1]. The simplest kind of models for adsorption are those defined in terms of random sequential adsorption (RSA) processes, in which particles of a given kind are adsorbed at random positions on the substrate. When the adsorption rates depend on the state of the neighbourhood of the position at which they take place, the process is known as cooperative sequential adsorption (CSA). A lattice version of the CSA process is monomer filling with nearest neighbour (NN) cooperative effects [1, 2]. These lattice models have been extensively used to study the monolayer growth of monodisperse particles. In particular, exact analytical solutions have been derived for the one-dimensional case [1].

The deposition of a mixture of different kinds of particles has also received some attention [3–11], but the progress made in its understanding is small as compared with the one-component problem. Here, a one-dimensional lattice model for a binary mixture of monomers with NN cooperative effects is considered and its analytical solution is found. Besides their theoretical interest, one-dimensional models are also useful for the description of some polymer reactions [1]. A controversial point in the adsorption of a mixture is whether it covers the substrate more or less efficiently than either of the species separately. Some results seemed to indicate that the former was true for lattice models [4, 9], while the latter applied for continuum models [8]. Nevertheless, a (continuum) random car parking model has been found to be consistent with the lattice models in this respect [10, 11]. For the lattice model considered here, it will be shown that the jamming coverage of the mixture is always between the coverage associated with each of the two components. This appears to be a direct consequence of the NN cooperative effects taken into account in the model.

It is interesting to note that lattice models with NN cooperative effects have also been considered in the context of Ising models. They were introduced by Fredrickson and Andersen [12–14] to study structural relaxation in glassy systems. In these models, a given spin can flip only if its nearest neighbours are in a certain subset of all their possible configurations and, because of this, they were termed 'facilitated' Ising models. In particular, in the so-called nSFM, one spin can flip only if at least n of its NN spins are orientated against the external field. It is easily verified that the zero-temperature limit of these models is the spin representation of the hole–particle (monomer) models mentioned above, i.e., both are related by a single change of variables. Interestingly, the one-dimensional 1SFM has also been used as a model to describe compaction process in vibrated granulates [15–17].

In the model considered in this paper, the two kinds of particles composing the mixture differ in their dynamics. Particles of one of the species obey RSA with NN exclusion or blocking [1], i.e., they can occupy an empty site with the constraint that both of its NN must be empty. On the other hand, adsorption of one particle of the other species on an empty site only requires that one of the NN be empty. Then, the dynamics of both kinds of particles is cooperative, but the 'facilitation' rules are different. A possible interpretation of this form of competitive adsorption is that particles are of the same size, but the effective repulsive interactions coming from the adsorbed particles are much stronger for one species than for the other. Then, the repulsive effect depends on the kind of particle trying to adsorb and on whether the NN sites are occupied or empty, but not on the type of particle actually occupying them.

In the next section, the model will be formulated in detail and the master equation describing its dynamics will be written down. The dynamics of the adsorption processes is studied in section 3, where explicit analytical expressions for the time evolution of the densities of each component are derived. For very large times, the system gets stuck in a jammed configuration, where no more adsorption events are possible. The asymptotic values of the densities of both species, as well as the total coverage, are also calculated as a function of the adsorption rate constants of the two species. It is found that the maximum asymptotic total coverage is always smaller than the one corresponding to the least repulsive particles. In order to get a deeper understanding of the stationary, jammed, state reached by the lattice in the long time limit, some correlation functions are analysed in section 4. The jammed states are characterized by having all the holes isolated, i.e., surrounded by two particles. Therefore, we will study the structure of the lattice around these isolated holes, analysing the probability of finding them between all the possible configurations of their NN sites. Section 5 contains a short summary of the main results and conclusions of the paper. Finally, some calculations are presented in the appendix.

2. The model

We consider two kinds of particles, A and B, that can be randomly adsorbed on a one-dimensional lattice. The adsorption processes on an empty site are restricted by the configuration of its NN, as follows:

(i) Particles A can be adsorbed on an empty site only if at least one of its NN is also empty.
(ii) Adsorption of a particle B on a site requires that both of the NN are empty.

Let us introduce two occupation numbers n_i and m_i for each site i of the lattice. If there is a particle A at site i, $n_i = 0$, otherwise $n_i = 1$. Similarly, $m_i = 1$ if there is a particle B at site i and $m_i = 0$ if there is not. Of course, since there can be at the most one particle at each site, $(1 - n_i)(1 - m_i) = 0$ for all i. A lattice configuration is specified by the sets of occupation numbers of the two species $\{\boldsymbol{n}, \boldsymbol{m}\}$, where $\boldsymbol{n} \equiv \{n_i\}$ and $\boldsymbol{m} \equiv \{m_i\}$.

The dynamics of the system is defined as a Markov process, so it is enough to specify the master equation for the probability distribution of the configurations, $p(\mathbf{n}, \mathbf{m}, t)$. As stated above, the elementary processes are the adsorption of particles A and B on an empty site i. In these events, the configuration of the system changes from $(\mathbf{n}, \mathbf{m})$ to $(R_i\mathbf{n}, \mathbf{m})$ or to $(\mathbf{n}, R_i\mathbf{m})$, depending on whether the adsorbed particle corresponds to species A or B. Here, R_i is the operator changing the occupation number n_i or m_i into $1 - n_i$ or $1 - m_i$, respectively. Thus, the master equation reads

$$\frac{\mathrm{d}}{\mathrm{dt}} p(\boldsymbol{n}, \boldsymbol{m}, t) = \sum_i [W_i(\boldsymbol{n}, \boldsymbol{m}|R_i\boldsymbol{n}, \boldsymbol{m}) p(R_i\boldsymbol{n}, \boldsymbol{m}, t) - W_i(R_i\boldsymbol{n}, \boldsymbol{m}|\boldsymbol{n}, \boldsymbol{m}) p(\boldsymbol{n}, \boldsymbol{m}, t)] \\ + \sum_i [W_i(\boldsymbol{n}, \boldsymbol{m}|\boldsymbol{n}, R_i\boldsymbol{m}) p(\boldsymbol{n}, R_i\boldsymbol{m}, t) - W_i(\boldsymbol{n}, R_i\boldsymbol{m}|\boldsymbol{n}, \boldsymbol{m}) p(\boldsymbol{n}, \boldsymbol{m}, t)], \tag{1}$$

where

$$W_i(R_i\boldsymbol{n}, \boldsymbol{m}|\boldsymbol{n}, \boldsymbol{m}) = \frac{\alpha}{2} n_i m_i (n_{i-1}m_{i-1} + n_{i+1}m_{i+1}), \tag{2}$$

$$W_i(\boldsymbol{n}, R_i\boldsymbol{m}|\boldsymbol{n}, \boldsymbol{m}) = \beta n_{i-1}m_{i-1}n_i m_i n_{i+1}m_{i+1}. \tag{3}$$

The above transition rates describe the adsorption of particles A and B on site i, respectively, consistent with rules (i) and (ii). The constant parameters α and β characterize the attempt frequency for each kind of adsorption process.

If $\alpha = 0$ or $\beta = 0$, the lattice will be occupied by particles of only one kind, and the dynamics of the model reduces to the one-component monomer filling with NN cooperative effects, whose solution is known and discussed in detail by Evans in [1]. When both rates are nonzero, we have the competitive adsorption of the two species: particles B need both of the NN sites of a given hole to be empty in order to adsorb, while one empty NN site is enough for a particle A. In the corresponding facilitated Ising picture [12–14], if $\beta = 0$ we have the one-dimensional 1SFM, while for $\alpha = 0$ the one-dimensional 2SFM is recovered.

We will restrict ourselves to translationally invariant states. This requires the consideration of consistent boundary conditions, e.g., periodic ones. In this case, the density of particles A at a given time t is given by

$$\rho_A(t) = 1 - \langle n_i \rangle_t, \tag{4}$$

where the angular brackets denote an average with the probability distribution $p(\mathbf{n}, m, t)$ and the right-hand site does not depend on the site i chosen. Similarly, the density of B particles is

$$\rho_B(t) = 1 - \langle m_i \rangle_t. \tag{5}$$

The total coverage of the line $\theta(t)$ is then

$$\theta(t) = \rho_A(t) + \rho_B(t). \tag{6}$$

It verifies $0 \leqslant \theta(t) < 1$, since it is impossible to fully fill the line, as will be discussed in detail later on. A particularly interesting property is the asymptotic coverage θ_J at jamming, i.e., once the system gets stuck in a configuration in which no more adsorption events are possible. In the model considered here, this happens when all the holes are isolated. Formally, we can write

$$\theta_J = \lim_{t\to\infty} \theta(t). \tag{7}$$

It is useful to consider the set of moments

$$F_r(t) = \langle n_i m_i n_{i+1} m_{i+1} \dots n_{i+r} m_{i+r} \rangle_t, \tag{8}$$

for all $r \geqslant 0$. They give the probability of finding $r + 1$ consecutive holes or, equivalently, the density of clusters of at least $r + 1$ empty sites. In particular, $F_0(t)$ gives the density of holes and, therefore, it must be

$$F_0(t) + \rho_A(t) + \rho_B(t) = 1. \tag{9}$$

The above equation can also be written as

$$\langle (1 - n_i)(1 - m_i) \rangle_t = 0, \tag{10}$$

expressing that a site cannot be simultaneously occupied by a particle A and a particle B. Besides, between each pair of particles B there must be at least one empty site, due to the adsorption rule for particles A. Therefore,

$$F_0(t) = 1 - \rho_A(t) - \rho_B(t) \geqslant \rho_B(t). \tag{11}$$

3. Analytical solution of the dynamics

Here, the consequences of the dynamics defined in the previous section will be analysed. First, the time evolution of the densities of both species will be investigated. Equations for them are readily obtained from the master equation (1),

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho_A(t) = \alpha F_1(t), \tag{12a}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho_B(t) = \beta F_2(t), \tag{12b}$$

where $F_1(t)$ and $F_2(t)$ are the densities of clusters with at least two and three consecutive holes, respectively, defined in equation (8). Also, a hierarchy of equations for all the marginal probabilities $F_r(t)$ is derived from the master equation,

$$\frac{\mathrm{d}}{\mathrm{d}t} F_0(t) = -\alpha F_1(t) - \beta F_2(t), \tag{13a}$$

$$\frac{\mathrm{d}}{\mathrm{d}t} F_r(t) = -(\alpha + 2\beta) F_{r+1}(t) - [\alpha r + \beta(r-1)] F_r(t), \qquad r \geqslant 1. \tag{13b}$$

Combination of equations (12) and (13a) implies that $F_0(t)+\rho_A(t)+\rho_B(t)$ is in fact an integral of motion, as required by equation (9). In order to solve the hierarchy of equations (13b), it is convenient to introduce the generating function

$$G(x, t) = \sum_{r=0}^{\infty} \frac{x^r}{r!} F_{r+1}(t), \tag{14}$$

such that

$$F_r(t) = \left(\frac{\partial^{r-1} G(x,t)}{\partial x^{r-1}} \right)_{x=0}, \qquad r \geqslant 1. \tag{15}$$

The generating function satisfies a linear first-order partial differential equation, namely

$$\partial_t G(x,t) + [\alpha + 2\beta + (\alpha+\beta)x]\partial_x G(x,t) = -\alpha G(x,t), \tag{16}$$

which has to be solved with the initial condition

$$G(x,0) = G_0(x) \equiv \sum_{r=0}^{\infty} \frac{x^r}{r!} F_{r+1}(0). \tag{17}$$

By using standard techniques, it is obtained that

$$G(x,t) = G_0 \left[-\frac{\alpha+2\beta}{\alpha+\beta} + \left(\frac{\alpha+2\beta}{\alpha+\beta} + x \right) \mathrm{e}^{-(\alpha+\beta)t} \right] \mathrm{e}^{-\alpha t}. \tag{18}$$

Then, from equation (15) we derive the whole set of moments $F_r(t)$ for $r \geqslant 1$,

$$F_r(t) = G_0^{(r-1)} \left[-\frac{\alpha+2\beta}{\alpha+\beta} + \left(\frac{\alpha+2\beta}{\alpha+\beta} \right) \mathrm{e}^{-(\alpha+\beta)t} \right] \mathrm{e}^{-\alpha r t}\, \mathrm{e}^{-\beta(r-1)t}, \tag{19}$$

where we have introduced the notation

$$G_0^{(r)}(x) \equiv \frac{\mathrm{d}^r G_0(x)}{\mathrm{d}x^r}. \tag{20}$$

In the long time limit $t \to \infty$, all the moments $F_r(t)$ such that $r \geqslant 1$ vanish, provided that $\alpha \neq 0$. This is easily understood: if adsorption of particles A is possible, the system evolves until it gets stuck in a metastable configuration such that all the holes are isolated, i.e., there are no pairs of consecutive holes. On the other hand, if $\alpha = 0$, so that only adsorption of particles B is allowed, $F_1(\infty) \neq 0$ while $F_r(\infty) = 0$ for $r \geqslant 2$. In the long time limit those configurations with at most two consecutive empty sites are jammed since, in order to adsorb on a given site, particles B need both of the nearest neighbours being empty. Therefore, the limit $\alpha \to 0$ must be handled with care in the present model, as the jammed configurations are different for $\alpha = 0$ and for $\alpha \to 0$ but not identically null.

The evolution equations for the densities of particles $\rho_A(t)$ and $\rho_B(t)$ are obtained by substituting equation (19) into equations (12),

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho_A(t) = \alpha G_0 \left[-\frac{\alpha+2\beta}{\alpha+\beta} + \frac{\alpha+2\beta}{\alpha+\beta}\, \mathrm{e}^{-(\alpha+\beta)t} \right] \mathrm{e}^{-\alpha t}, \tag{21a}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho_B(t) = \beta G_0' \left[-\frac{\alpha+2\beta}{\alpha+\beta} + \frac{\alpha+2\beta}{\alpha+\beta}\, \mathrm{e}^{-(\alpha+\beta)t} \right] \mathrm{e}^{-(2\alpha+\beta)t}. \tag{21b}$$

These equations must be integrated to get explicit expressions for the densities $\rho_A(t)$ and $\rho_B(t)$. In order to do this, we have to specify the initial condition for the generating function $G_0(x)$ or, equivalently, the complete set of marginal probabilities $F_r(0)$.

For the sake of concreteness, we will consider that the lattice is empty at $t = 0$. This is the usual initial state in adsorption studies. Therefore,

$$F_r(0) = 1, \qquad \forall r \geqslant 0, \tag{22}$$

and, as a consequence,

$$G_0(x) = \sum_{r=0}^{\infty} \frac{x^r}{r!} = \mathrm{e}^x. \tag{23}$$

From equation (19), we get

$$F_r(t) = \exp\left[-\frac{\alpha+2\beta}{\alpha+\beta} + \frac{\alpha+2\beta}{\alpha+\beta}\,\mathrm{e}^{-(\alpha+\beta)t} - \alpha r t - \beta(r-1)t\right], \tag{24}$$

for $r \geqslant 1$. In the long time limit $t \to \infty$,

$$F_r(\infty) = \lim_{t\to\infty} F_r(t) = 0, \qquad \forall r \geqslant 1, \tag{25}$$

provided that $\alpha \neq 0$, consistently with the above general discussion. As already indicated, for $\alpha = 0$ the adsorption of particles A is impossible, and, in general, $F_1(\infty) \neq 0$. Use of equation (24) in equation (21) yields

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho_A(t) = \alpha \exp\left[-\frac{\alpha+2\beta}{\alpha+\beta} + \frac{\alpha+2\beta}{\alpha+\beta}\,\mathrm{e}^{-(\alpha+\beta)t} - \alpha t\right], \tag{26a}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho_B(t) = \beta \exp\left[-\frac{\alpha+2\beta}{\alpha+\beta} + \frac{\alpha+2\beta}{\alpha+\beta}\,\mathrm{e}^{-(\alpha+\beta)t} - (\alpha+2\beta)t\right]. \tag{26b}$$

These equations can be integrated, with the result

$$\rho_A(t) = \frac{1}{1+r}\,\mathrm{e}^{-\frac{1+2r}{1+r}} \int_{\mathrm{e}^{-(\alpha+\beta)t}}^{1} \mathrm{d}u\, u^{-\frac{r}{1+r}}\, \mathrm{e}^{\frac{1+2r}{1+r}u}, \tag{27a}$$

$$\rho_B(t) = \frac{r}{1+r}\,\mathrm{e}^{-\frac{1+2r}{1+r}} \int_{\mathrm{e}^{-(\alpha+\beta)t}}^{1} \mathrm{d}u\, u^{\frac{1}{1+r}}\, \mathrm{e}^{\frac{1+2r}{1+r}u}, \tag{27b}$$

where we have introduced the ratio of the attempt frequencies of adsorption

$$r = \frac{\beta}{\alpha}. \tag{28}$$

Integration by parts of equation (27*b*) gives an explicit relationship between both densities $\rho_A(t)$ and $\rho_B(t)$,

$$\rho_B(t) = \frac{r}{1+2r}\left\{1 - \mathrm{e}^{-\alpha t}\,\mathrm{e}^{\frac{1+2r}{1+r}[\mathrm{e}^{-(\alpha+\beta)t}-1]} - \rho_A(t)\right\}. \tag{29}$$

Let us analyse the long time limit of the densities, when the system gets jammed in a metastable configuration and no more adsorption events are possible. In this limit, the densities tend to the values

$$\rho_A(\infty) = \frac{1}{1+r}\,\mathrm{e}^{-\frac{1+2r}{1+r}} \int_0^1 \mathrm{d}u\, u^{-\frac{r}{1+r}}\, \mathrm{e}^{\frac{1+2r}{1+r}u}, \tag{30a}$$

$$\rho_B(\infty) = \frac{r}{1+r}\,\mathrm{e}^{-\frac{1+2r}{1+r}} \int_0^1 \mathrm{d}u\, u^{\frac{1}{1+r}}\, \mathrm{e}^{\frac{1+2r}{1+r}u}, \tag{30b}$$

which are related by

$$\rho_B(\infty) = \frac{r}{1+2r}[1 - \rho_A(\infty)], \tag{31}$$

as long as $\alpha \neq 0$. In the long time limit, the tendencies to these asymptotic limits are

$$\rho_A(\infty) - \rho_A(t) \sim \mathrm{e}^{-\frac{1+2r}{1+r}}\,\mathrm{e}^{-\alpha t}, \tag{32a}$$

$$\rho_B(\infty) - \rho_B(t) \sim \frac{r}{2+r}\,\mathrm{e}^{-\frac{1+2r}{1+r}}\,\mathrm{e}^{-(2\alpha+\beta)t}. \tag{32b}$$

Both types of behaviour are exponential, but the characteristic time $(2\alpha+\beta)^{-1}$ for particles B is smaller than the characteristic time α^{-1} for particles A. Thus, the total coverage of the line $\theta(t)$, defined by equation (6), verifies

$$\theta_J - \theta(t) = \rho_A(\infty) - \rho_A(t) + \rho_B(\infty) - \rho_B(t) = \mathrm{e}^{-\frac{1+2r}{1+r}}\,\mathrm{e}^{-\alpha t} + \mathcal{O}[\mathrm{e}^{-(2\alpha+\beta)t}], \tag{33}$$

where θ_J is the total coverage at jamming, given by equation (7). The asymptotics of the coverage is dominated by the contribution of particles A. This is easily understood, since as time increases a configuration will be reached where no more adsorption of particles B is possible. On the other hand, particles A can still be adsorbed on the lattice. Our results show that this situation will be found for times of the order of $(2\alpha+\beta)^{-1}$, for which $\rho_B(t)$ has already decayed to $\rho_B(\infty)$ while $\rho_A(t)$ is still evolving. This exponential approach near the jamming limit is characteristic of any adsorption process in a one-dimensional lattice. Power-law convergence, like Feder's t^{-1} law [18], arises when continuous deposition is considered [19, 20].

In the limit $r \to \infty$ $(\alpha \ll \beta)$, equation (30*b*) leads to

$$\lim_{r\to\infty} \rho_B(\infty) = \tfrac{1}{2}(1-\mathrm{e}^{-2}), \tag{34}$$

and, therefore,

$$\lim_{r\to\infty} \rho_A(\infty) = 1 - 2\lim_{r\to\infty} \rho_B(\infty) = \mathrm{e}^{-2}, \tag{35}$$

which is nonzero. On the other hand, for $\alpha = 0$ we know that $\rho_A(t) = 0$ for all t. This shows again the singularity of the case $\alpha = 0$. For any $\alpha \neq 0$, the system gets stuck in configurations characterized by having all the holes isolated, while for $\alpha = 0$ those configurations having, at most, two consecutive holes are also metastable. The adsorption of particles A on a previously jammed configuration of particles B is analysed in the appendix. In that situation, the asymptotic density of particles A, equation (A.11), equals equation (35). For $\alpha \to 0$ but nonzero, the system first reaches, over a time scale of the order of β^{-1}, a jammed configuration with only particles B. Afterwards, for times of the order of $\alpha^{-1} \gg \beta^{-1}$, particles A are adsorbed on this state, leading to an asymptotic density of particles A given by equation (35). The asymptotic total coverage, defined in equation (7), in the limit case we are considering is

$$\lim_{r\to\infty} \theta_J = \lim_{r\to\infty} [\rho_A(\infty) + \rho_B(\infty)] = \tfrac{1}{2}(1+\mathrm{e}^{-2}), \tag{36}$$

which also equals equation (A.12), as expected on the basis of the discussion above.

The limit $r \to 0$, i.e., $\beta \to 0$ does not present any kind of singularity. For $r = 0$ it is readily obtained that

$$\lim_{r\to 0} \rho_A(\infty) = 1 - \mathrm{e}^{-1}, \qquad \lim_{r\to 0} \rho_B(\infty) = 0. \tag{37}$$

The system only contains particles A, and the result agrees with the one obtained for the one-component system [1].

As would be expected on physical grounds, the asymptotic density of particles $\rho_B(\infty)$ is a monotonic increasing function of r, while $\rho_A(\infty)$ decreases with r. A plot of both asymptotic densities as a function of the adsorption rates ratio r is shown in figure 1. The jamming coverage can be written in terms of $\rho_A(\infty)$ by using equation (31),

$$\theta_J = \rho_A(\infty) + \rho_B(\infty) = \frac{r}{1+2r} + \frac{1+r}{1+2r}\rho_A(\infty), \tag{38}$$

which is a decreasing function of r, varying from

$$\lim_{r\to 0} \theta_J = 1 - \mathrm{e}^{-1} \simeq 0.63 \tag{39}$$

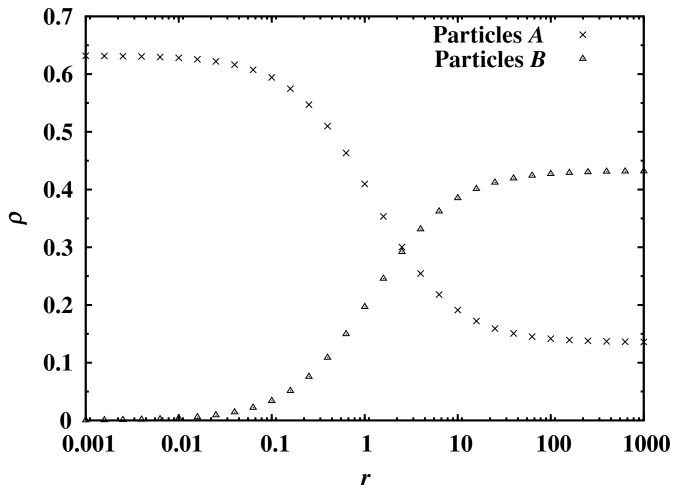

Figure 1. Plot of the asymptotic densities $\rho_A(\infty)$ (crosses) and $\rho_B(\infty)$ (triangles) as a function of the adsorption rates ratio r. Note that $\lim_{r\to\infty} \rho_A(\infty) \neq 0$, as expressed by equation (35).

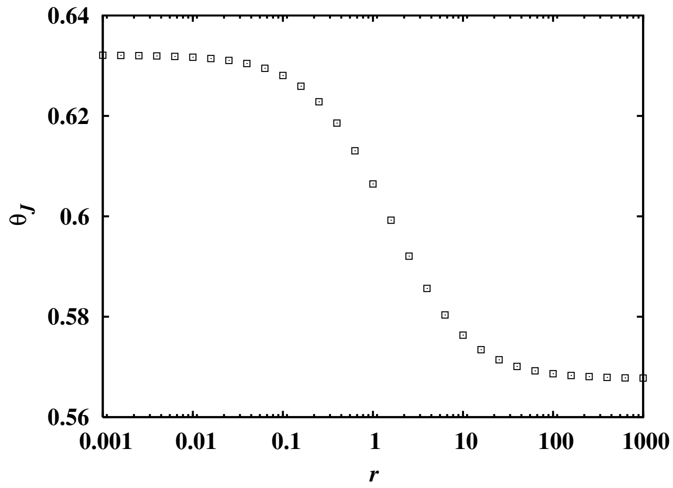

Figure 2. Plot of the asymptotic total coverage θ_J as a function of r.

to

$$\lim_{r\to\infty} \theta_J = \tfrac{1}{2}(1 + \mathrm{e}^{-2}) \simeq 0.57. \tag{40}$$

Figure 2 shows the total coverage θ_J as a function of r. The maximum value of the coverage is obtained for $r \to 0$ ($\beta \to 0$), i.e., when the adsorption of particles B is forbidden, and there are only particles A in the system. This is reasonable on physical grounds: due to the facilitation rule, the domain between two particles B cannot be completely full of particles A. Therefore, the density of particles B is a lower bound for the density of holes. As the density of particles B increases with $r = \beta/\alpha$, the asymptotic density of holes $F_0(\infty)$ also increases with r and the jamming coverage θ_J decreases, since $\theta_J = 1 - F_0(\infty)$. This behaviour is in contrast to all the previous results for RSA in continuum parking models [8, 10, 11] and in lattice models [9, 4]. In these works, it is reported that the substrate is covered either less or more efficiently by a binary mixture than by a single species. The model presented here, however, leads to binary coverage lying between that of the two monodisperse cases. This is a consequence of the cooperativity of the adsorption processes taking place in our system.

4. Correlations

In order to get a more complete description of the steady state, we have also investigated some correlation functions. In the steady state, holes are isolated, i.e., surrounded by two particles. In particular, we will be interested in the structure of the lattice surrounding these isolated holes. In the previous section, the time evolution of the total hole density $F_0(t)$ has been found, and here the density of holes for a given configuration of their two nearest neighbours will be studied. In the asymptotic stationary state, they can be both particles A (AA), one particle A and one particle B (AB or BA), and two particles B (BB). Let us define the density

$$\Phi_0^{AA}(t) = \langle (1-n_{i-1})m_{i-1}n_im_i(1-n_{i+1})m_{i+1}\rangle_t, \tag{41}$$

that corresponds to the density of empty sites surrounded by two particles A. In a similar way, we introduce

$$\Phi_0^{AB}(t) = \langle (1-n_{i-1})m_{i-1}n_im_in_{i+1}(1-m_{i+1})\rangle_t, \tag{42}$$

$$\Phi_0^{BA}(t) = \langle n_{i-1}(1-m_{i-1})n_im_i(1-n_{i+1})m_{i+1}\rangle_t, \tag{43}$$

$$\Phi_0^{BB}(t) = \langle n_{i-1}(1-m_{i-1})n_im_in_{i+1}(1-m_{i+1})\rangle_t, \tag{44}$$

corresponding to the density of holes between a particle A on the left and a particle B on the right $\left(\Phi_0^{AB}\right)$, etc. In the jammed state,

$$F_0(\infty) = \Phi_0^{AA}(\infty) + \Phi_0^{AB}(\infty) + \Phi_0^{BA}(\infty) + \Phi_0^{BB}(\infty). \tag{45}$$

Nevertheless, an analogous expression does not hold for arbitrary time t, since then it is possible to find configurations with two adjacent holes. This is clear from the fact that the moments $F_r(t)$, with $r \geqslant 1$, do not vanish except in the limit $t \to \infty$. Then, the asymptotic fraction of holes between two particles A at jamming is

$$x_J^{AA} = \frac{\Phi_0^{AA}(\infty)}{F_0(\infty)}. \tag{46}$$

Similarly, we define

$$x_J^{AB} = \frac{\Phi_0^{AB}(\infty)}{F_0(\infty)}, \tag{47}$$

as the relative density of holes between a particle A to the left and a particle B to its right,

$$x_J^{BA} = \frac{\Phi_0^{BA}(\infty)}{F_0(\infty)}, \tag{48}$$

which gives the relative density of holes between a particle B to the left and a particle A to its right, and

$$x_J^{BB} = \frac{\Phi_0^{BB}(\infty)}{F_0(\infty)}, \tag{49}$$

for the fraction of holes between two particles B.

The evolution equations for these moments are again readily obtained from the master equation. For the density of holes between two particles A, one gets

$$\frac{\mathrm{d}}{\mathrm{d}t}\Phi_0^{AA}(t) = \alpha\left[\Phi_2^A(t) + \Phi_3^A(t)\right], \tag{50}$$

where

$$\Phi_r^A(t) = \langle n_i m_i n_{i+1} m_{i+1} \ldots n_{i+r-1} m_{i+r-1}(1-n_{i+r}) m_{i+r}\rangle_t, \tag{51}$$

i.e., it is the probability of finding r consecutive holes from site i onwards and a particle A on site $i+r$. These probabilities obey the hierarchy of equations

$$\frac{\mathrm{d}}{\mathrm{d}t}\Phi_r^A = -\left(\frac{\alpha}{2}+\beta\right)\Phi_{r+1}^A - [\alpha(r-1)+\beta(r-2)]\Phi_r^A + \frac{\alpha}{2}(F_r + F_{r+1}), \tag{52}$$

for $r \geqslant 2$. For an arbitrary initial condition, this hierarchy of equations can be solved by a generating function method analogous to the one used to integrate the evolution equations for $F_r(t)$, in spite of the inhomogeneous term proportional to $F_r + F_{r+1}$. Nonetheless, for the initially empty lattice configuration, it is simpler to assume that

$$\Phi_r^A(t) = \xi_A(t)\,\mathrm{e}^{-[\alpha(r-1)+\beta(r-2)]t}. \tag{53}$$

This time dependence is suggested by the hierarchy of equations (52) and, also, by the time dependence of the inhomogeneous term, which is precisely of this form, as follows from equation (24). By substituting equation (53) into equation (52), a differential equation for $\xi_A(t)$ follows

$$\frac{\mathrm{d}\xi_A}{\mathrm{d}t} = -\left(\frac{\alpha}{2}+\beta\right)\mathrm{e}^{-(\alpha+\beta)t}\xi_A + \frac{\alpha}{2}\exp\left[-\frac{\alpha+2\beta}{\alpha+\beta} + \frac{\alpha+2\beta}{\alpha+\beta}\,\mathrm{e}^{-(\alpha+\beta)t}\right]\mathrm{e}^{-(\alpha+\beta)t}[1+\mathrm{e}^{-(\alpha+\beta)t}]. \tag{54}$$

This is easily integrated, with the result

$$\xi_A(t) = \frac{2\alpha\beta}{(\alpha+2\beta)^2}\exp\left[-\frac{\alpha+2\beta}{2(\alpha+\beta)} + \frac{\alpha+2\beta}{2(\alpha+\beta)}\,\mathrm{e}^{-(\alpha+\beta)t}\right] + \frac{\alpha}{\alpha+2\beta}\exp\left[-\frac{\alpha+2\beta}{\alpha+\beta} + \frac{\alpha+2\beta}{\alpha+\beta}\,\mathrm{e}^{-(\alpha+\beta)t}\right]\left[\frac{\alpha}{\alpha+2\beta} - \mathrm{e}^{-(\alpha+\beta)t}\right]. \tag{55}$$

Thus, we have identified all the moments $\Phi_r^A(t)$ and, by using equation (50), obtain the following closed evolution equation for $\Phi_0^{AA}(t)$:

$$\frac{\mathrm{d}}{\mathrm{d}t}\phi_0^{AA}(t) = \alpha\xi_A(t)\,\mathrm{e}^{-\alpha t}[1+\mathrm{e}^{-(\alpha+\beta)t}]. \tag{56}$$

Since the lattice was initially empty, $\Phi_0^{AA}(t=0) = 0$, and

$$\Phi_0^{AA}(t) = \frac{2r}{(1+r)(1+2r)^2}\,\mathrm{e}^{-\frac{1+2r}{2(1+r)}}\int_{\mathrm{e}^{-(\alpha+\beta)t}}^{1}\mathrm{d}u\, u^{-\frac{r}{1+r}}(1+u)\,\mathrm{e}^{\frac{1+2r}{2(1+r)}u} + \frac{1}{(1+r)(1+2r)}\,\mathrm{e}^{-\frac{1+2r}{1+r}}\int_{\mathrm{e}^{-(\alpha+\beta)t}}^{1}\mathrm{d}u\, u^{-\frac{r}{1+r}}(1+u)\left(\frac{1}{1+2r}-u\right)\mathrm{e}^{\frac{1+2r}{1+r}u}, \tag{57}$$

where r was defined in equation (28). Therefore, the asymptotic density of holes surrounded by two particles A is

$$\Phi_0^{AA}(\infty) = \frac{2r}{(1+r)(1+2r)^2}\,\mathrm{e}^{-\frac{1+2r}{2(1+r)}}\int_0^1\mathrm{d}u\, u^{-\frac{r}{1+r}}(1+u)\,\mathrm{e}^{\frac{1+2r}{2(1+r)}u} + \frac{1}{(1+r)(1+2r)}\,\mathrm{e}^{-\frac{1+2r}{1+r}}\int_0^1\mathrm{d}u\, u^{-\frac{r}{1+r}}(1+u)\left(\frac{1}{1+2r}-u\right)\mathrm{e}^{\frac{1+2r}{1+r}u}. \tag{58}$$

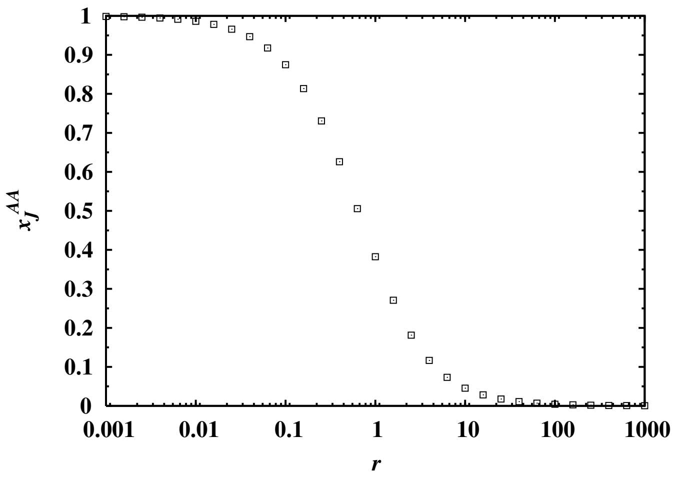

Figure 3. Plot of the relative density $x_J^{AA}(\infty)$ (squares) as a function of the adsorption rates ratio r (in a logarithmic scale).

In the limit $r \to 0$, this equation reduces to

$$\lim_{r\to 0} \Phi_0^{AA}(\infty) = \mathrm{e}^{-1} \int_0^1 \mathrm{d}u (1+u)(1-u)\,\mathrm{e}^u = \mathrm{e}^{-1} = \lim_{r\to 0} F_0(\infty). \tag{59}$$

This is readily understood, as the limit $r \to 0$ corresponds to $\beta = 0$, in which no adsorption events for particles B are possible. On the other hand, in the limit $r \to \infty$,

$$\lim_{r\to\infty} \Phi_0^{AA}(\infty) = 0. \tag{60}$$

This result may appear as nontrivial, since it must be stressed that when $r \to \infty$ there is a finite, nonvanishing, density of particles A in the steady state, given by equation (35). Nevertheless, as discussed below that equation, the adsorption of particles A takes place for very long times $t = \mathcal{O}(\alpha^{-1}) \gg \beta^{-1}$, on sites with at most one empty nearest neighbour. As the latter must be next to a particle B, it follows that Φ_0^{AA} vanishes for $r \to \infty$. In figure 3, the fraction of holes between two particles A, x_J^{AA}, defined in equation (46), is plotted as a function of r. It decreases monotonically from unity for $r = 0$ to zero for $r \to \infty$, as expected.

Let us now analyse the density of holes between two particles B, $\Phi_0^{BB}(t)$. From the master equation, it is obtained

$$\frac{\mathrm{d}}{\mathrm{d}t}\Phi_0^{BB} = 2\beta\Phi_3^B, \tag{61}$$

where now

$$\Phi_r^B(t) = \langle n_i m_i n_{i+1} m_{i+1} \ldots n_{i+r-1} m_{i+r-1} n_{i+r}(1 - m_{i+r})\rangle_t, \tag{62}$$

i.e., it is the probability of finding r consecutive holes from site i onwards and a particle B on site $i + r$. Note the analogy of the notation used here with the one introduced for the moments Φ_r^A defined in equation (51). These moments obey the hierarchy

$$\frac{\mathrm{d}}{\mathrm{d}t}\Phi_r^B = -\left(\frac{\alpha}{2} + \beta\right)\Phi_{r+1}^B - [\alpha(r-1) + \beta(r-2)]\Phi_r^B + \beta F_{r+1}, \tag{63}$$

for $r \geqslant 2$. Again, for the initially empty lattice we are considering, the family of solutions

$$\Phi_r^B(t) = \xi_B(t)\,\mathrm{e}^{-[\alpha(r-1)+\beta(r-2)]t} \tag{64}$$

can be considered. Substitution of the above expression into equation (63) yields a closed differential equation for $\xi_B(t)$, namely

$$\frac{\mathrm{d}}{\mathrm{d}t}\xi_B = -\left(\frac{\alpha}{2}+\beta\right)\mathrm{e}^{-(\alpha+\beta)t}\xi_B + \beta\exp\left[-\frac{\alpha+2\beta}{\alpha+\beta}+\frac{\alpha+2\beta}{\alpha+\beta}\,\mathrm{e}^{-(\alpha+\beta)t}\right]\mathrm{e}^{-2(\alpha+\beta)t}, \tag{65}$$

which can be integrated by standard techniques, obtaining

$$\xi_B(t) = \frac{4\beta(\alpha+\beta)}{(\alpha+2\beta)^2}\exp\left[-\frac{\alpha+2\beta}{\alpha+\beta}+\frac{\alpha+2\beta}{\alpha+\beta}\,\mathrm{e}^{-(\alpha+\beta)t}\right]\left[1-\frac{\alpha+2\beta}{2(\alpha+\beta)}\,\mathrm{e}^{-(\alpha+\beta)t}\right] - \frac{2\alpha\beta}{(\alpha+2\beta)^2}\exp\left[-\frac{\alpha+2\beta}{2(\alpha+\beta)}+\frac{\alpha+2\beta}{2(\alpha+\beta)}\,\mathrm{e}^{-(\alpha+\beta)t}\right]. \tag{66}$$

This provides the expressions for all the densities Φ_r^B $(r \geqslant 2)$, from equation (64). Taking into account equation (61) and the initial condition, it is found

$$\Phi_0^{BB}(t) = \frac{8r^2}{(1+2r)^2}\,\mathrm{e}^{-\frac{1+2r}{1+r}}\int_{\mathrm{e}^{-(\alpha+\beta)t}}^{1}\mathrm{d}u\,u^{\frac{1}{1+r}}\left[1-\frac{1+2r}{2(1+r)}u\right]\mathrm{e}^{\frac{1+2r}{1+r}u} - \frac{4r^2}{(1+r)(1+2r)^2}\,\mathrm{e}^{-\frac{1+2r}{2(1+r)}}\int_{\mathrm{e}^{-(\alpha+\beta)t}}^{1}\mathrm{d}u\,u^{\frac{1}{1+r}}\,\mathrm{e}^{\frac{1+2r}{2(1+r)}u}. \tag{67}$$

In the long time limit,

$$\Phi_0^{BB}(\infty) = \frac{8r^2}{(1+2r)^2}\,\mathrm{e}^{-\frac{1+2r}{1+r}}\int_0^1\mathrm{d}u\,u^{\frac{1}{1+r}}\left[1-\frac{1+2r}{2(1+r)}u\right]\mathrm{e}^{\frac{1+2r}{1+r}u} - \frac{4r^2}{(1+r)(1+2r)^2}\,\mathrm{e}^{-\frac{1+2r}{2(1+r)}}\int_0^1\mathrm{d}u\,u^{\frac{1}{1+r}}\,\mathrm{e}^{\frac{1+2r}{2(1+r)}u}. \tag{68}$$

If the adsorption of particles B is forbidden, $\beta \to 0$ or $r \to 0$, the expected result,

$$\lim_{r\to 0}\Phi_0^{BB}(\infty) = 0, \tag{69}$$

is obtained. On the other hand, when there is no adsorption of particles A, $\alpha \to 0$ or $r \to \infty$,

$$\lim_{r\to\infty}\Phi_0^{BB}(\infty) = 2\,\mathrm{e}^{-2}\int_0^1\mathrm{d}u(1-u)\,\mathrm{e}^{2u} = \frac{1}{2}-\frac{3}{2}\,\mathrm{e}^{-2}. \tag{70}$$

Then, $\Phi_0^{BB}(\infty)$ does not equal the total density of holes $F_0(\infty)$ in this limit. This is due to the fact that for $\alpha \neq 0$, although very small, there is a nonvanishing density of particles A, given by equation (35). The consistent result is

$$\lim_{r\to\infty}\left[F_0(\infty)-\Phi_0^{BB}(\infty)\right] = \lim_{r\to\infty}\rho_A(\infty). \tag{71}$$

As we have already discussed above, in the limit $r \to \infty$ particles A are adsorbed once the system has reached a jammed configuration in which only particles B have been adsorbed $(\alpha = 0)$. These intermediate configurations are characterized by having clusters of holes involving at most two consecutive sites. Therefore, particles A will be adsorbed in one of the empty sites of those clusters with two adjacent holes, i.e.,

$$\lim_{r\to\infty}\left[\Phi_0^{BB}(\infty)+\rho_A(\infty)\right] = \lim_{r\to\infty}F_0(\infty), \tag{72}$$

because $\rho_A(\infty)$ equals the density of holes between a particle B and another hole in the intermediate 'metastable' state. In figure 4, the fraction of holes between two particles B, x_J^{BB}, is plotted as a function of the adsorption rates ratio r. It is seen that x_J^{BB} is a monotonically increasing function of r. It must be noted that $\lim_{r\to\infty}x_0^{BB} \neq 1$, since in that limit $F_0^{BB}(\infty)$ does not equal the total density of holes $F_0(\infty)$, as expressed by equation (72). More concretely,

$$\lim_{r\to\infty}x_J^{BB} = \lim_{r\to\infty}\frac{F_0^{BB}(\infty)}{F_0(\infty)} = \frac{1-3\,\mathrm{e}^{-2}}{1-\mathrm{e}^{-2}}. \tag{73}$$

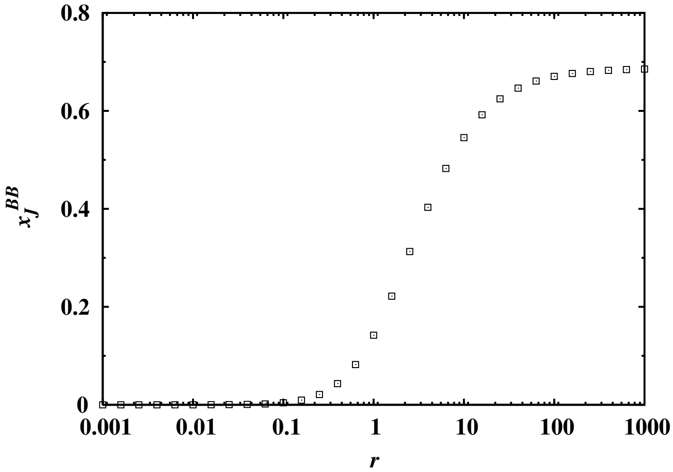

Figure 4. Plot of the concentration x_J^{BB} as a function of r (on a logarithmic scale). Note that x_J^{BB} does not tend to unity for $r \to \infty$.

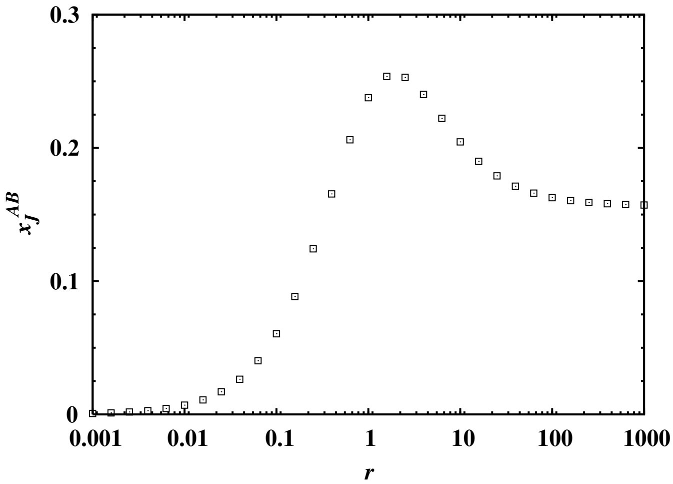

Figure 5. Plot of $x_J^{AB}(\infty)$ as a function of r (on a logarithmic scale). A maximum occurs for $r \simeq 2$.

Taking into account equation (45), it is possible to obtain also the density of holes between one particle A and one particle B, independently of their relative positions

$$\Phi_0^{AB}(\infty) = \Phi_0^{BA}(\infty) = \tfrac{1}{2}\left[F_0(\infty) - \Phi_0^{AA}(\infty) - \Phi_0^{BB}(\infty)\right]. \tag{74}$$

The fraction of holes between two distinct particles $x_J^{AB} = x_J^{BA}$ is plotted in figure 5. It has a non-monotonic behaviour, exhibiting a maximum for $r \simeq 2$, i.e., in the region where the attempt rates of adsorption α and β are of the same order of magnitude. For $r \to 0$, $x_J^{AB} \to 0$, since no particles B are adsorbed on the lattice. On the other hand, in the limit $r \to \infty$ a 'minimum' adsorption of particles A is required on those groups of two consecutive holes left by the previous adsorption of particles B, as already discussed. Then,

$$\lim_{r\to\infty} x_J^{AB} = \lim_{r\to\infty} \frac{\Phi_0^{AB}(\infty)}{F_0(\infty)} = \lim_{r\to\infty} \frac{\rho_A(\infty)}{2F_0(\infty)} = \frac{\mathrm{e}^{-2}}{1-\mathrm{e}^{-2}}, \tag{75}$$

since in that limit $\Phi_0^{AB} + \Phi_0^{BA} = 2\Phi_0^{AB}$ should equal ρ_A, as expressed by equations (71) or (72).

5. Conclusions

The objective here has been to study a one-dimensional model for the adsorption of a binary mixture on a lattice with nearest neighbour cooperative effects. Both species are of the same size (monomers), but they differ in the strength of the NN repulsive interactions, as measured by the number of NN empty sites required for a particle to adsorb. Emphasis has been put on the jammed configuration reached by the system in the long time limit. The asymptotic coverage of the lattice by the mixture differs from previous results both for the random sequential adsorption of mixtures on lattices and continuous substrates [4, 8–11]. The mixture always covers the lattice more efficiently than the species of particles feeling stronger NN repulsion and less efficiently than the species experiencing a weaker one. In fact, the jamming coverage is a monotonic function of the ratio between the attempt rates of adsorption for the two species. This is a consequence of the cooperativity of the adsorption events considered in our model.

In the long time limit, the tendency to the asymptotic value of the coverage is dominated by the least cooperative species. This is similar to the behaviour observed in models with species of different sizes, in which this approach is dominated by the smaller species [4, 8–11]. Nevertheless, in our model the approach is exponential and, therefore, Feder's t^{-1} power law [18] does not hold. This is a consistent result, since exponential behaviour is characteristic of any d-dimensional lattice deposition, evolving to a power law when a continuum deposition limit is introduced [19, 20].

The structure of the jamming configuration has also been investigated by computing some spatial correlation functions. Here, the interest has been in the nature of the holes, i.e., the kind of particles surrounding them. The relative densities of holes between two identical particles, of either of the two species, show a monotonic behaviour as a function of the adsorption rates ratio. On the other hand, the fraction of holes between two particles of different species displays a maximum in the region where both attempt rates of adsorption are of the same order of magnitude. This may be relevant information in order to determine the properties of the adsorbed layer in a given physical system.

The model discussed here is closely related to the so-called facilitated Ising models, first introduced by Fredrickson and Andersen [12–14]. The main characteristic of these systems is that, although their thermal equilibrium properties are trivial, their dynamics is highly cooperative and very slow. A recent review on these kinetically constrained Ising models can be found in [21]. They are appropriate and have been used to model physical systems such as structural glasses [14, 22–24] or dense granulates [15, 25–29], in which the structural rearrangement of a given region may be slowed down or even blocked by the configuration of the surroundings.

Irreversible cooperative adsorption processes have also been used as models for the free relaxation between two shakes in vibration experiments with granular systems [15, 25–29]. Let us consider a horizontal section of a real granular binary mixture, near the bottom of its container. During the free evolution of the system, i.e., only under the action of gravity, particles can only go down, as long as there is enough empty space in their surroundings.

The total density of particles in the layer grows until the hard-core interaction prevents more movements of particles and a *metastable* (mechanically stable) configuration is reached. Different kinds of grains may also need different amounts of free space in their surroundings to be adsorbed on or desorbed from the layer. In our system, these kinetic constraints are modelled by the different 'facilitation rules' for the adsorption of both species. On the other hand, when the system is submitted to vertical vibration, particles can go up, decreasing the density in the layer. This vibration dynamics can be modelled by allowing desorption events. In this way, a simple model to analyse granular segregation phenomena in a binary mixture can be formulated [17].

Acknowledgments

This research was supported by the Ministerio de Educación y Ciencia (Spain) through grant no FIS2005-01398 (partially financed by FEDER funds).

Appendix A. Adsorption of particles A on a jammed configuration of particles B

In this appendix, we will briefly analyse the dynamics of a system in which particles A adsorb on a jammed state corresponding to a previous adsorption of particles B. The adsorption of B particles is equivalent to the one-dimensional RSA with NN exclusion or blocking, whose solution is well known [1]. In the jammed state of particles B, the density of holes reads

$$F_0(\infty) = \tfrac{1}{2}(1 + \mathrm{e}^{-2}), \tag{A.1}$$

and the density of pairs of consecutive holes is

$$F_1(\infty) = \mathrm{e}^{-2}. \tag{A.2}$$

Since the jammed state of particles B is characterized by having at most two consecutive holes,

$$F_r(\infty) = 0 \qquad \text{for all } r \geqslant 2. \tag{A.3}$$

The asymptotic density of particles B directly follows from the density of holes,

$$\rho_B(\infty) = 1 - F_0(\infty) = \tfrac{1}{2}(1 - \mathrm{e}^{-2}). \tag{A.4}$$

Let us now consider that this jammed state for the system of particles B is the initial state for the adsorption of particles A. Therefore, in terms of the moments $F_r(t)$ we will have

$$F_r(0) = 0, \qquad \forall r \geqslant 2; \qquad F_1(0) \neq 0, \qquad F_0(0) \neq 0, \tag{A.5}$$

$F_0(0)$ and $F_1(0)$ being the initial density of holes and of pairs of consecutive holes, given by equations (A.1) and (A.2), respectively. Besides, the initial densities of particles are

$$\rho_A(0) = 0, \qquad \rho_B(0) \neq 0, \tag{A.6}$$

where $\rho_B(0)$ is given by equation (A.4).

In order to solve this problem, the formalism developed for the complete system in section 3, making $\beta = 0$, can be used. The initial generating function is

$$G_0(x) = \sum_{r=0}^{\infty} \frac{x^r}{r!} F_{r+1}(0) = F_1(0), \tag{A.7}$$

which is independent of x. Then, equation (19) yields

$$F_1(t) = F_1(0)\,\mathrm{e}^{-\alpha t}, \tag{A.8}$$

i.e., the density of pairs of consecutive holes decays exponentially. Of course, $F_r(t) = 0$ for all $r \geqslant 2$. The evolution equations for the densities (21) are very simple,

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho_B(t) = 0, \qquad \frac{\mathrm{d}}{\mathrm{d}t}\rho_A(t) = \alpha F_1(0)\,\mathrm{e}^{-\alpha t}, \tag{A.9}$$

leading to

$$\rho_A(t) = F_1(0)(1 - \mathrm{e}^{-\alpha t}). \tag{A.10}$$

This result reflects that the initial configuration is a jammed state of the particles B and, therefore, the holes are either isolated or in groups of two consecutive holes, whose density is $F_1(0)$. Particles A can be adsorbed on any of the $2F_1(t)$ sites which are next to a hole, with a rate $\alpha/2$. As all of these processes are independent, the density of hole pairs $F_1(t)$ decays exponentially as $\exp(-\alpha t)$ and the density of particles A also increases exponentially until it reaches its steady value

$$\rho_A(\infty) = F_1(0) = \mathrm{e}^{-2}, \tag{A.11}$$

with a characteristic time $\tau = \alpha^{-1}$. Note that this is precisely the limit of $\rho_A(\infty)$ when $r = \beta/\alpha \to \infty$ (equation (35)). Besides, the total coverage of the line will be

$$\theta_J = \rho_A(\infty) + \rho_B(\infty) = \tfrac{1}{2}(1 + \mathrm{e}^{-2}), \tag{A.12}$$

which agrees with equation (36).

References

[1] Evans J W 1993 *Rev. Mod. Phys.* **65** 1281
[2] Keller J B 1963 *J. Chem. Phys.* **38** 325
[3] Talbot J and Schaaf P 1989 *Phys. Rev.* A **40** 422
[4] Bartelt M C and Privman V 1991 *Phys. Rev.* A **44** R2227
[5] Meakin P and Jullien R 1992 *Phys. Rev.* A **46** 2029
[6] Brilliantov N V, Andrienko Y A, Kaprivski P L and Kurths J 1996 *Phys. Rev. Lett.* **76** 4058
[7] Pastor-Satorras R 1999 *Phys. Rev.* E **59** 5701
[8] Bonnier B 2001 *Phys. Rev.* E **64** 066111
[9] Bonnier R 1992 *Europhys. Lett.* **18** 297
[10] Hassan M K, Schmidt J, Blasius B and Kurths J 2002 *Physica* A **315** 163
[11] Hassan M K, Schmidt J, Blasius B and Kurths J 2002 *Phys. Rev.* E **65** 045103
[12] Fredrickson G H and Andersen H C 1984 *Phys. Rev. Lett.* **53** 1244
[13] Fredrickson G H and Andersen H C 1985 *J. Chem. Phys.* **83** 5822
[14] Fredrickson G H and Brawer S A 1986 *J. Chem. Phys.* **84** 3351
[15] Brey J J, Prados A and Sánchez-Rey B 1999 *Phys. Rev.* E **60** 5685
[16] Prados A, Brey J J and Sánchez-Rey B 2000 *Physica* A **284** 277
[17] Prados A and Brey J J 2003 *Europhys. Lett.* **64** 29
[18] Feder J and Giaever I 1980 *J. Colloid Interface Sci.* **78** 144
[19] Pomeau Y 1980 *J. Phys. A: Math. Gen.* **13** L193
[20] Swendsen R H 1981 *Phys. Rev.* A **24** 504
[21] Ritort F and Söllich P 2003 *Adv. Phys.* **52** 219
[22] Butler S and Harrowell P 1991 *J. Chem. Phys.* **95** 4454
[23] Butler S and Harrowell P 1991 *J. Chem. Phys.* **95** 4466
[24] Reiter J and Jackle J 1995 *Physica* A **215** 311
[25] Brey J J, Prados A and Sánchez-Rey B 2000 *Physica* A **275** 310
[26] Lefevre A and Dean D S 2001 *J. Phys. A: Math. Gen.* **34** L213
[27] Berg J, Franz S and Sellitto M 2002 *Eur. Phys. J.* B **26** 349
[28] Smedt G D, Godreche C and Luck J M 2002 *Eur. Phys. J.* B **27** 363
[29] Prados A and Brey J J 2002 *Phys. Rev.* E **66** 041308