Segregation in a noninteracting binary mixture

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Process of stripe formation is analyzed numerically in a binary mixture. The system consists of particles of two sizes, without any direct mutual interactions. Overlapping of large particles, surrounded by a dense system of small particles, induces indirect entropy driven interactions between large particles. Under an influence of an external driving force the system orders and stripes are formed. Mean width of stripes grows logarithmically with time, in contrast to a typical power law temporal increase observed for driven interacting lattice gas systems. We describe the mechanism responsible for this behavior and attribute the logarithmic growth to a random walk of large particles in a random potential created by the site blocking due to the small ones.

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I. INTRODUCTION

Binary mixtures subject to an external driving force are often found to segregate and form stripes whose width is increasing with time [1–4]. Separation of mechanically agitated mixtures of different characteristics has important practical applications in the processing of granular materials in chemical or pharmaceutical technology. Much theoretical and experimental work has been done in order to understand the main mechanisms responsible for these processes [5–10]. The simplest and best known model for stripe formation under external driving force is a simple lattice gas with attractive nearest neighbor interparticle interactions [11–13]. Recent experiments [14–16] have rejuvenated interest in that model.

In this paper we propose a model for a stripe formation in a lattice gas model with two kinds of particles, which generalizes the standard driven one-component model. As we shall see the presence of the second particle component modifies the time evolution of the system considerably. When two types of particles differ in their sizes, the entropy driven phase separation might occur and no direct interaction between particles is necessary for particles to cluster [17–19]. In our model we assume existence of two lattice gas components consisting of small and large particles which occupy one or more lattice sites depending on the specific rules which might allow for particles to overlap. Specifically, we assume that small particles occupy one lattice site and do not share it with other small and/or large ones, while large particles extend over five lattice sites and are permitted to overlap. This rule leads to the blocking phenomenon for small particles which in turn results in an effective interaction between large particles [18,19] and the system orders at high enough densities. This ordering happens because the large particles perform the random walk in a random potential. A jump of the large particle can occur only when there is enough free space in a chosen direction, the latter being a random event. We will show that this difference from the conventional driven lattice gas is sufficient to result in a different time growth of the stripes than that described in the previous literature [7,12]. Indeed we shall show that the mean stripe width in our model increases logarithmically with time.

II. STRIPE FORMATION IN THE BINARY SYSTEM

Stripe formation can be easily observed in a simple lattice gas model with nearest neighbor attractive interactions. It has been shown [11–13] by means of Monte Carlo (MC) simulations that such a system orders in stripes under an influence of external driving force. When the evolution starts from some random particle configuration, stripes are formed: Initially they are thin; they gradually become thicker. This process, described and analyzed in detail in Refs. [5–9], occurs in two stages—stripe formation and then stripe growth. The mean width of stripes grows typically as a power of a simulation time t^x (where time is measured in the number of MC steps). Typically, two different powers $x=1/3$ and $x=1/4$ are observed depending on the system size and the simulation time [7].

In this paper we will study the segregation process in a binary mixture of noninteracting particles. The system consists of large objects occupying five lattice sites each and a large number of small objects occupying one lattice site only. Double occupancy of the core site in the middle of a large particle is forbidden, while the other four sites can be shared with other large ones. Small particles occupy one site and cannot share it with any other particles. When large particles overlap they leave more free sites for small particles so the "phase space," i.e., the number of possible configurations for that species, increases. This effectively creates attractive forces between large particles due to higher entropy of macrostates with overlapping particles. This is why the system orders forming stripes, when driven by either the periodic in time or static external force.

The kinetics of our model follows the rules differently for large and small particle species in our lattice gas. To execute a jump for a large particle we first choose randomly one of four possible lattice directions. Then occupation of sites at each of these directions is checked. The particle moves only if other particles (large or small) do not block it. The large particles move randomly with the same jump probability in each direction. Once the direction of the jump is selected and it is not blocked then the probability of a jump is always set to $p=1$. That holds also if there is an external force—a bias applied to the system. The jump probability p is independent

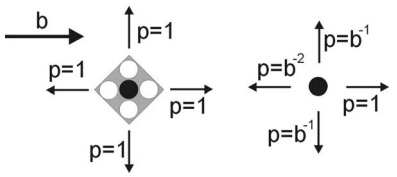

FIG. 1. Jump rules for large (left) and for small (right) particles. White sites can be shared by overlapping large particles. The external bias b affects the jump rates of small particles only.

of the direction of the bias. For small particles the situation is different. The biasing field determines the jump rate and that influence is measured by the parameter b. Specifically, when a small particle tries to jump it checks whether the direction of the jump is not blocked. If it is not and it happens to be in the direction of the bias field then the jump probability is set to $p=1$. If that direction is opposite to the bias field than the jump probability is set to b^{-2}. If the jump direction happens to be perpendicular to the bias field, then the jump probability is set equal to b^{-1}. We found it proper to use $b=5$ in most of our analysis. Figure 1 presents the jump rules for large and small particles. To analyze the time evolution of our model we have studied systems of different lattice sizes under the periodic boundary conditions applied in both system directions. In each sample the number of large particles N is kept fixed. We allow the number of small particles to change; therefore, we have been able to study both closed and open systems, respectively. The system is closed when the number N_s of small particles is kept constant, which means that free volume increases during stripe formation. To study the open system we allow small particles to adsorb and desorb in such a way that their mean density ρ_s is kept constant. Such a possibility is realized in one additional step per site during the simulation process. To keep the small particles density constant we apply the following procedure: We choose a random lattice site. If it is empty we put there an additional small particle with the probability $p_A=0.01\rho_s$. That is an act of "adsorption." If the chosen lattice site is already occupied by a small particle we remove it (desorption) with the probability $p_D=0.01(1-\rho_s)$. The adsorbed particle continues then to jump following the standard rule for small particle jump as shown in Fig. 1. The coefficient 0.01, in definition of p_A and p_D, makes adsorption and desorption processes much slower than the particle diffusion over the lattice plane.

Although there is no direct (that is mediated by the force fields) interaction between particles of our binary mixture the constraints described above on the occupation of the lattice sites by large and small particle results in the fact that the particle configurations in which large particles are closer to each other occurs with relatively higher probability. It has been shown in Refs. [18,19] that this fact allows us to map our model onto an Ising model with an effective nearest-neighbor interaction. Strength of this effective interaction depends on the density of the small particles ρ_s. The strength of this interaction increases with the density ρ_s and, eventually, at critical density, a phase transition occurs. This effective, entropic in origin, interaction together with the biasing field leads to a formation of stripes parallel to the external bias field. As we observe, systems that are studied here form

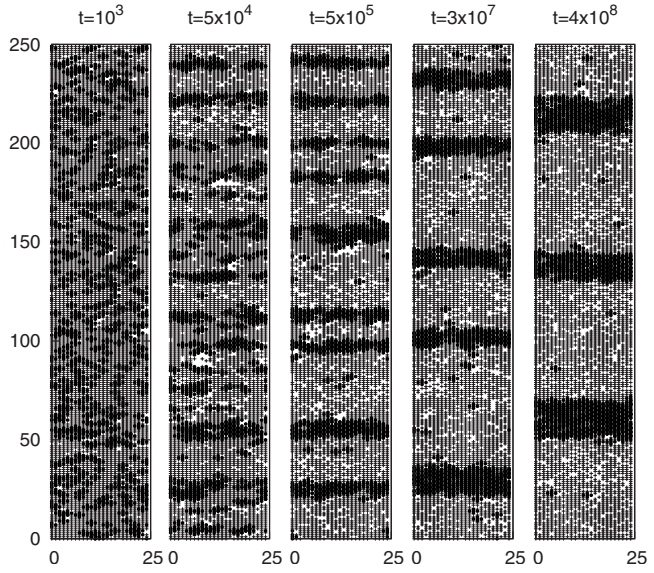

FIG. 2. Successive stages of separation of large (dark) and small (light) particles. Free sites are visible as white spots. The biasing field is parallel to the shorter side of the system. System size is (25×250). It is populated by 500 large and 3972 small particles and closed, i.e., number of particles, both large and small, does not change during simulation. The initial free sites fraction is 0.01.

stripe structure when density is over $\rho_s^c\sim0.69$. In Fig. 2 we have shown snapshots of our binary mixture configurations drawn at various time steps. Here and in what follows time is measured in the number of the Monte Carlo steps leading to that configuration.

For a closed system, increasing fraction of (unoccupied by either particles) free space is a signature of an ordering process. Ratio m of the number of free sites to the total number of sites as a function of time t is plotted in Fig. 3. At $t>10^4$ the curve shows a steplike structure. Each step lasts a relatively long period of time (note logarithmic time scale in the main panel of Fig. 3) during which the number of stripes

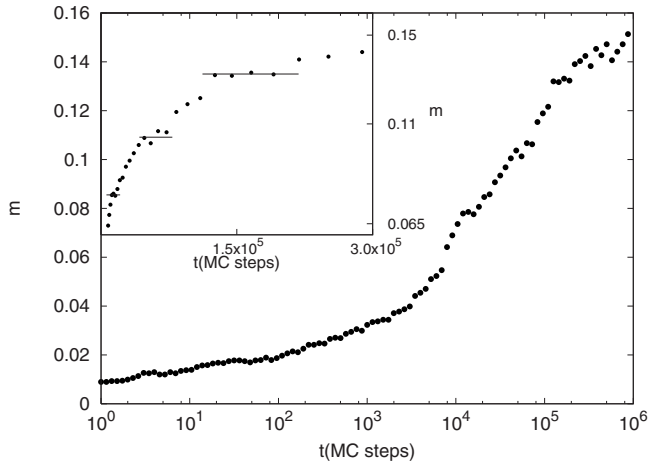

FIG. 3. Fraction of free sites m in the closed system as a function of time for one sample. System size is (25×250) sites populated by 500 large and 3972 small particles. The initial free sites fraction is 0.01. Inset presents the part of data with step structure in linear scale.

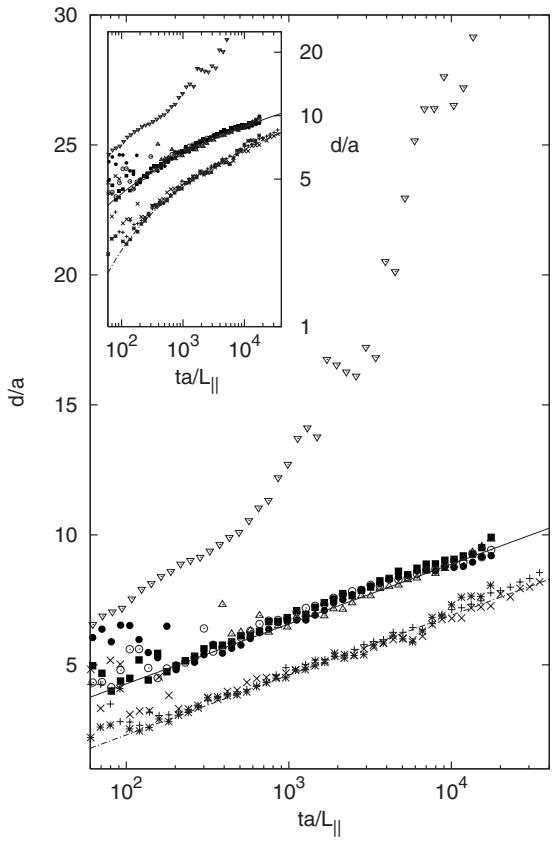

FIG. 4. Rescaled mean stripe width $d=\kappa l$ as a function of rescaled time for closed, open, and interacting systems in log-linear (main panel) and log-log plots. See text for explanations for scale κ; a is a lattice constant.

does not change. These steps can be observed when there are only a few stripes present in the system. When a new step shows up at the curve in Fig. 3 it indicates that one of the spatial stripes disappears. For open systems, density of small particles, hence also averaged number of free sites in the system, is constant. Average number of stripes decreases with time t and their average width $l(t)$ increases with time, as seen in Fig. 4.

Similar to Refs. [6,7] we observe two stages of stripe width growth. The first stage begins when clusters of large particles coarsen and ends when individual stripes length becomes comparable to the system size and a multistripe structure becomes clearly visible. The second stage begins when the stripes are already well formed and continues when the stripes are merging together. Two consecutive evolution stages of the stripes in the closed system are shown in Fig. 3 and correspond to gentle and steep slopes of the graph. We conclude from that figure that for closed systems the number of unoccupied sites increases with time during stripe growth and subsequently saturates reaching maximum when the system finally separates into two parts. In open systems the number of free sites fluctuates around constant mean value, whereas the number of small particles increases up to its maximal value in a completely phase separated system.

We now show results of our Monte Carlo simulations for closed and open systems, of various width-to-height ratio and for different numbers of large particles and varying number of small particles in closed systems. For open systems the small particles are kept at varying particle densities. For each system we analyze, we have averaged the results over the sample of 100 different realizations. In each of those realizations the initial distribution of the large particles was randomized allowing those particles overlap. Subsequently, we placed small particles over a fraction of the remaining empty lattice sites again at random. Having generated the particular arrangements of the large and small particles, we have turned on the bias field and performed the usual Monte Carlo simulation procedure. In the analysis of the results we compared data obtained for closed systems, with a fixed number of small particles, with those for the open systems of fixed external potential controlling the small particle density. Formation of structures was monitored at two different realizations of the bias field: The static one and the one whose direction was changing periodically with time. The rate of stripe formation was highest for a constant field, and it decreases with an increasing frequency of the field variation. The results do not change qualitatively until a frequency of around 1/5 (MC steps) is reached, above which stripes for each of the configuration of particles stop to form at all. For that reason most of our results shown here are for constant in time driving force.

To find an average width of the stripes for a given configuration of particles, a correlation function

$$f_c(r) = \begin{cases} \frac{1}{2N}\sum_{[i,j]} n_i n_j & \text{for } |r| = 0, \\ \frac{1}{4N}\sum_{[i,j]} n_i n_j & \text{for } |r| \neq 0 \end{cases} \tag{1}$$

was evaluated where $|r|$ is the distance between ith and jth site along the direction perpendicular to the external field and $n_i, n_j = 0, 1$ are the occupations of ith and jth site, respectively. n_i is equal to 1 when the site i is occupied by one or more large particles and $n_i=0$ otherwise. N is the number of large particles. In Eq. (1) the sum runs over all sites whose perpendicular to stripes coordinates differ by $|r|$. The average width of the stripes is that value of $|r|$ at which the correlation function $f_c(r)$ has the first minimum.

The analysis of our simulation results indicates that the mean width of stripes grows as a logarithm of time independently of the system size. This is shown in Fig. 4. This figure contains results grouped in seven data sets. Six of them refer to the presently studied two-component systems and the seventh one, shown for comparison, is for the one component system, described in Refs. [12,13]. The main panel in Fig. 4 shows the mean width of stripes l as a function of $\log(t)$. Three lower data sets, labeled with $*$, $+$, and $\times$, represent results obtained for systems with a fixed number of small particles. The remaining data sets labeled with ■, ○, ●, and △ represent results for open systems, with fixed external potential, shown in the center of the figure.

In each of these graphs the stripe width l was rescaled by a factor κ chosen such that each data set lies on the same line

$$d = \kappa l = \log\left(\frac{t}{\alpha L_{\parallel}}\right), \tag{2}$$

where $L_{\parallel}$ is the system width, parallel to stripes ($L_{\parallel}=25$ was chosen as in Fig. 2). Two different values of the coefficient α were used to shift the data without changing the slope of the plot. We have chosen $\alpha=10$ for closed and $\alpha=1.4$ for open systems. The scaling factor κ in Eq. (2) depends on the density of the free sites $m=N_V/(L_{\parallel}L_{\perp})$. Since for open systems N_V changes in time we have used for m its mean value from the second stage of the stripe growth. For closed systems $\kappa=\sqrt{m_{\text{averaged}}}/4$, and for open systems $\kappa=\sqrt{m_{\text{averaged}}}/2.8$.

In all our simulations we have used systems with different sizes labeled with (*)—(100×50), (+)—(100×25), and (×)—(250×25). The number of large particles were $N=600$, 300, and 781, respectively. At the beginning of simulation small particles occupy 99% of available space; then the number of free sites increases (see Fig. 3). For open systems shown in Fig. 4 the size of each of them is (100×25), $N=300$ and the external potential was chosen such that the small particle mean density is equal to 80% ■ (full squares), 85% ○ (open circles), 90% ● (full circles), and 95% △ (triangles) of the number of sites available to them at any time.

The upper set labeled by inverted triangles ▽ represents the stripe growth for a one-component interacting driven system at a temperature $0.8T_c^{\infty}$, where $T_c^{\infty}=3.18J/k_B$ (where $J=1$ is interaction strength) and jump probabilities: $p=1$ in the direction of field, $p=0$ in the opposite direction, and $p=\exp(-cJ/T)$ in the direction perpendicular to the field, where c is the number of nearest neighbors. As shown in Refs. [6,7], in such a system the width of the stripe increases as $t^{1/4}$ or $t^{1/3}$ (cf. inset in Fig. 4). The curve labeled with ▽ shows the stripe growth proportional to $t^{1/4}$ at the early stage, which changes behavior to $t^{1/3}$ at the later stage.

With those results plotted next to each other we can compare the behavior of the one-component interacting and driven system with the behavior for noninteracting similarly driven system results. As shown in Fig. 4 the stripes are formed for each of those systems but the third mode of growth is quite different. In contrast to the power law growth observed for interacting systems the stripe growth in the binary mixture case, caused by the entropic interactions, is much slower and indeed logarithmic. Ordering in the binary system happens due to the indirect, effective attractive interaction between particles. Strength of this entropic interaction decreases with increasing number of free sites [18]. That is exactly the reason why for the closed systems the effective interaction between particles decreases (cf. Fig. 3) To see how the change of the strength of effective interactions affects the stripe growth, we have checked the behavior of the open systems in which the mean number of small particles was controlled by fixing those particles chemical potential. In that case when a stripe is formed more small particles can be absorbed to the system due to the fixed value of their chemical potential. The effective interaction between large particles changes then in a fashion different from the closed system case. As shown in Fig. 4, however, the time dependence in an open system has the same logarithmic character observed for the closed system.

We conclude, therefore, that the crucial feature of the observed time evolution for the stripes is the existence of two different kind of particles. In order to cross an interstripe distance, large particles have to find their way through densely packed small ones. To execute a jump, the large particle has to wait until a channel opens for it in the cloud of the small particles filling the space between the large particle and the stripe. A passing stream of small particles creates a hole, large enough to fit in. As a waiting time for a jump in such case varies from one event to the next, we can treat such a process as a random walk in a random potential. In the next section, we show that the logarithmic character of the temporal stripe width growth can be explained by such a description of large particles kinetics.

III. MECHANISM OF STRIPE GROWTH

Stripe growth is an anisotropic process that takes place in the driven systems. The main course of growth happens along the direction perpendicular to stripes. Existence of the second dimension controls relative probabilities of several mechanisms that compete in the stripe growth process. This process in a one-component system has been analyzed and explained in detail in Refs. [6,7]. Reference [7] describes two different competing mechanisms: Evaporation and condensation of particles from the surface of the stripe and diffusion of particles and holes between interfaces. The former one leads to $l\sim t^{1/4}$ and can be observed at earlier times or for shorter systems, whereas the latter leads to the $l\sim t^{1/3}$ growth and is activated at later stages of stripe formation or in longer systems.

Let us consider a one-component system with particles attracting each other. The system orders under influence of a static bias field, initially forming many thin stripes. When the process continues some of the stripes disintegrate while the remaining ones become thicker. Stripe extinction is a random process consisting of a single particle action: A particle evaporates first from the stripe wall, then walks randomly in an empty space until it readsorbs at the same or the other wall. The process continues until the stripe disintegrates. Decay of one of two neighboring stripes is a problem similar to that of the gambler ruin [20]. We are interested in the mean time of ultimate decay of the one of two neighboring stripes. This time is proportional to the mean time of evaporation of one particle row across a given stripe. The number of particles in such a row is proportional to the width of the stripe and fluctuates as particles escape from and come back to the stripe. The occurrence of a fluctuation of size l means that a row of such length disappears. The mean time τ for such an event scales as l^2. Fluctuations occur independently in each row, so the time in which the entire stripe disappears is proportional to the number of rows in one stripe, $L_{\parallel}$, and to the time τ_0 needed for a single particle to pass the distance from one stripe to another. If the distance between stripes becomes longer, in the space of stripes there is more than one large

particle per row. Thus mean time between the events, when a large particle reaches the stripe, becomes shorter. It should be corrected by the mean number of large particles in empty space per row n_0. The number n_0 will be set to 1, as long as there is one or no particles between stripes, and for higher densities $n_0 \sim s$. Thus we write

$$\tau = \nu \frac{1}{n_0} L_\parallel \tau_0 l^2, \tag{3}$$

where ν is an overall time scale parameter.

Consider now the mean first-passage time of a distance between stripes by a particle τ_0. In the general case of an inhomogeneous potential the first-passage time is given by [21,22]

$$\tau_0 = \sum_{n=0}^{s-1} \frac{1}{p_n} \sum_{k=n}^{s-1} \prod_{j=n}^{k} \frac{q_j}{p_j}, \tag{4}$$

where p_j is the jump rate from site j in the direction pointing from the initial site 0 to the final site s and q_j is the jump rate in the opposite direction. The mean distance between stripes depends on the density of large particles ρ in the system and can be written as $s = l(1-\rho)/\rho$. For the one-component system we can assume that $p_j = q_j$ in Eq. (4) and that p_j are the same for all $j = 1, \ldots, s$ except when $j = 0$ for a jump originating at a site neighboring the stripe. The rate p_0 is a probability rate for a jump of one of the particles that are neighbors. The particles attract each other, so this rate is smaller than all others: $p_0 < p_1$. We can write

$$\tau_0 \sim \frac{s}{p_0} + \frac{s^2}{p_1} \tag{5}$$

and treat p_0 as an effective rate averaged over many jumps. If $p_0/p_1 < s$, then the second term of Eq. (5) dominates. For larger value of s we use $n \sim s$ and

$$\tau \sim \nu \frac{s}{p_1} L_\parallel l^2. \tag{6}$$

Equation (6) is valid if the density of particles between stripes is higher than one particle per row but is still quite low. For higher densities, however, pair interactions in the empty space start to play a role, causing the entire process to slow down even more.

A stripe of width l disappears in time τ given by Eq. (3) which means that all its particles move to other still existing stripes. Hence the mean speed of the equation of motion for the stripe growth is equal l/τ and the stripe growth can be written as

$$\frac{dl}{dt} = \frac{l}{\tau} = \frac{n_0}{\nu L_\parallel l \tau_0(l)}. \tag{7}$$

The solution of this equation for τ_0 given in Eq. (5) and $n_0 = 1$ is

$$\frac{(1-\rho) l^3}{3 p_0 \rho} + \frac{l^4 (1-\rho)^2}{4 p_1 \rho^2} \sim \frac{t}{L_\parallel}. \tag{8}$$

The exponent of the power law growth of l changes between 1/3 and 1/4. When $n \sim s$ and Eq. (6) is used, we get

$$l \sim \left(\frac{t}{L_\parallel} \right)^{1/3}, \tag{9}$$

i.e., the power law time dependence with a single exponent $x = 1/3$ [7]. For higher temperatures when particle density between stripes becomes higher, various values of exponent x, usually smaller than 1/3, are observed. Still, $l \sim t^{1/3}$ is a dominant behavior for a wide range of temperatures and system geometry parameters.

When the system consists of two different types of particles, random walk from one stripe to another is not free. Each particle has to wait until there is enough space for it to jump. We can treat the process of particle motion in a dense medium as a random walk in a random potential landscape. A jump to the left with rate p_l and jump to the right with rate p_r are in this approach independent events, occurring according to the same probability distribution. Such a model leads to the following expression for the mean first-passage time [21]

$$\tau_0 \sim \frac{2\gamma(\gamma^s - 1)}{(\gamma - 1)^2} \sim e^{\lambda l}, \tag{10}$$

where

$$\gamma = \langle p_l \rangle \left\langle \frac{1}{p_r} \right\rangle > 1, \tag{11}$$

with $\langle\ \rangle$ being an average over random variable realizations. Thus all linear in s terms in expression (10) are irrelevant for large s and we get $\lambda = \log(\gamma)(1-\rho)/\rho$. Using now Eqs. (3) and (10) and $n_0 \sim s$ we get the following equation:

$$\frac{dl}{dt} \sim \frac{e^{-\lambda l}}{L_\parallel}. \tag{12}$$

Its solution for large l and t can be written as

$$l \sim \log(t/L_\parallel) \tag{13}$$

and, indeed, such character of the time dependence is observed in Fig. 4 for binary systems. It can be seen in the inset of Fig. 4 that the power law cannot be fitted to the data sets for binary mixtures. The character of stripe growth is the same for a closed system, where the number of free sites increases, as it is for an open system with constant density of small particles controlled by external potential.

IV. SUMMARY

We have investigated a binary mixture system driven by an external force. Particles in this binary system do not interact with each other directly but they effectively do so via indirect entropic interaction. In binary systems large particles travel among densely packed small particles, which effectively slows down their wandering. The system orders form-

ing stripes, like a driven single component system with attractive forces.

The existence of two different particle types in the presented system leads to the logarithmic temporal growth of the mean stripe width. Such time dependence is slower than the power law temporal growth in an interacting one-component system.

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