PHYSICAL REVIEW E VOLUME 55, NUMBER 3 MARCH 1997

Role of diffusion in irreversible deposition

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(Received 23 May 1996)

The adsorption of spheres onto solid surfaces is investigated using a cellular automaton model of diffusion deposition. Unlike previous models, the diffusive transport of the particles from the bulk to the surface as well as their interaction with adsorbed particles are explicitly considered at a microscopic level. We study the initial time regime, which determines the subsequent evolution and during which the particle flux at the surface is not constant. We observe that diffusion-driven adsorption differs significantly from random sequential adsorption (RSA) when particles diffuse in a two-dimensional bulk and are adsorbed on a one-dimensional substrate. We also find that the microscopic details of the diffusive motion influence both the kinetics of deposition and the jamming limit of the coverage. The RSA model appears to be a good approximation, especially for two-dimensional deposition, but cannot generally represent diffusion deposition. [S1063-651X(97)05103-9]

PACS number(s): 68.45.Da, 82.20.Mj, 05.20.−y, 02.70.Rw

I. INTRODUCTION

The adsorption of proteins and other particles at the solid-liquid interface is a widespread process of fundamental importance in nature. Since many of these adsorption processes are partly or wholly irreversible, kinetic measurements assume a particular importance for their investigation. Recently, the advent of accurate experimental techniques [1] has increased interest in the theoretical description of the process since verification becomes possible.

The basic ingredients of an irreversible adsorption process are (i) transport of the particle from the bulk to the proximity of the surface and (ii) subsequent adsorption onto the surface. Among the large number of possible interactions that may play a specific role, we focus on the hard-sphere interactions between preadsorbed and bulk particles. The most studied model that includes the surface exclusion effect is that of random sequential adsorption (RSA) (see [2] for a review).

The RSA model is characterized by sequential deposition attempts of particles of unit area at a constant rate c per unit time and area. Adsorption occurs only under the condition that there is no resulting overlap. The coverage evolution ends up in a jammed state in which no gaps large enough to admit further particle remain. Even though RSA goes deeper into the description of adsorption processes than previous models such as the Langmuir isotherm [3], it cannot be entirely correct since coupling between deposition and transport is neglected. Hence recent theoretical [4,5] and numerical [6,7] works have focused on the effect of diffusion on the kinetics of deposition and the structure of the asymptotic jammed configuration and have established departures from the RSA predictions.

Nevertheless, a complete description of the diffusion-adsorption (DA) process is still needed. In particular, very little is known about the initial adsorption regime. Yet the early-time behavior is expected to play an important role in the process because the way the first particles are adsorbed will determine the late spatial coverage structure. Any departure from the RSA jamming limit must be due to the initial buildup of the deposit. However, the asymptotic rate of deposition is expected to correspond to RSA dynamics because in the long-time regime the remaining positions where adsorption is still possible are sparse enough for deposition attempts from the bulk to be decorrelated.

In this paper, we investigate the dynamics and the structure of the deposit in a diffusion-driven adsorption process and we compare it to the RSA process. Our study is based on a cellular automaton model of diffusion for the particles in the bulk. On the other hand, the deposition substrate is a continuum and the excluded volume is treated in its full generality during the adsorption phase. Note that, contrary to previous work, our dynamics are not sequential and we may have simultaneous adsorption of many particles.

The remainder of this paper is organized as follows. Section II describes our cellular automaton model for diffusion controlled adsorption. Section III presents the numerical simulations actually carried out. Section IV analyzes the results. Concluding remarks appear in Section V.

II. MODEL

Cellular automaton (CA) modeling has already been successfully applied to various problems in physics such as fluid flows [8], surface reaction models [9], and reaction-diffusion phenomena [10–13]. Here we couple a CA model for the

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*Electronic address: [luthi/chopard]@cui.unige.ch transport of particles in the bulk with an adsorption mechanism for the deposition on the surface. The behavior of the bulk particles is supposed to be purely diffusive and other possible effects such as hydrodynamic interactions [14] are neglected.

Diffusion is modeled as a synchronous random walk on a square lattice of unit mesh size, as described in [15]. The square lattice is bounded on one side by the surface of deposition, whereas the opposite side acts as a source of particles with a constant concentration ρ (density of particles per site). Periodic boundary conditions are applied to the other sides.

On a two-dimensional lattice the random walk is produced by rotating the velocity of the particles by an angle $\alpha_i \in \{0, \pi/2, \pi, -\pi/2\}$ chosen at random with probability p_i, independently for each site of the lattice. For instance, p_2 denotes the probability for the sites to reverse the speed of their incoming particles ($\alpha_2 = \pi$) and thus play the role of a perfect reflector. $p_1 = p_3 = p$ are the probabilities for a ±90° scattering. Finally, p_0 is the probability of no deviation. The diffusion constant D of the particle motion is determined as [15]

$$D = (p_0 + p)/[4(1 - p - p_0)] \tag{1}$$

in lattice units.

Unlike the bulk diffusion, the deposition (adsorption) takes place in a continuum. To achieve this, we shift the boundary lattice layer next to the surface of deposition by a uniform value $\delta_\mathbf{r}$ randomly chosen at each time step, with $|\delta_\mathbf{r}|$ uniformly distributed in the interval $[-1/2, +1/2]$. Thus the effective deposition attempts occur at positions $\mathbf{r}_i + \delta_\mathbf{r}$, where $\mathbf{r}_i$ denotes the integer coordinates of the ith lattice boundary site occupied by a particle traveling towards the surface. Undoubtedly we have introduced some correlations between particles adsorbing at the same time, but we believe these correlations are not important when dealing with small concentrations. A constant probability q controls the adsorption of a particle provided there is no overlap with previously adsorbed particles. Once adsorbed, the particle leaves the lattice; otherwise it is maintained at the same lattice site with an equal and opposite velocity as if it had rebounded from the surface (see Fig. 1). The particles are assumed to be spherical for convenience, with radius 1/4.

To summarize, a small set of parameters fully determines our model: the dimensions of the lattice N_x $(\times N_y) \times N_z$ for line (surface) deposition; the initial concentration ρ of the bulk in particles per site; the diffusion constant D as determined by the choice of $p0, p1, p2, p3$ ($p0, p1, p2, p3, p4, p5$), given in [15]; and finally q, the probability for adsorption to actually take place. Physically, q may account for various physicochemical effects hindering adsorption such as electrostatic repulsion, hydration repulsion, or selective molecular recognition.

III. TIME AND PARAMETERS

There are two major reasons why a DA process differs from the predictions of a RSA model: (i) temporal evolution and (ii) correlations of the deposition rate. The first is easily eliminated by appropriately choosing how time is measured. For a RSA process, time is naturally the total number of deposition attempts per unit surface, but for a DA process time is naturally defined through the diffusion phenomena. In order to make significant comparisons between RSA and DA we choose to define a generalized dimensionless *deposition time* τ as the the average cumulative sum of deposition attempts per unit surface from the begining of the process up to the observed (laboratory) time t,

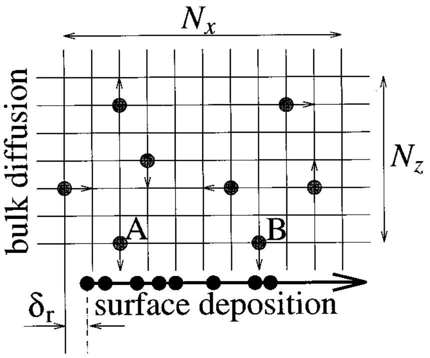

FIG. 1. Discrete diffusion on the lattice and continuum deposition on the surface. $\delta_\mathbf{r}$ is randomly chosen at each time step and shifts all deposition attempts occurring at that time step. The deposition is accepted only if there is no resulting overlap (case A); otherwise the particle stays on the lattice with equal and opposite velocity as if it were reflected by the preadsorbed particles (case B).

$$\tau = \int_0^t du \frac{\sigma}{S} \int_\Sigma dx\, c(x,u), \tag{2}$$

where c is the microscopic deposition rate, σ is the area occupied by an adsorbed particle, and S is the area of the deposition surface Σ initially available.

If c were homogeneous over space, corresponding to a mean-field time-dependent deposition rate $c(t)$, the DA process would be indistinguishable from the RSA process, provided that the appropriate renormalization had been carried out, but this is not the case, as will be shown in Sec. IV. For RSA, both the kinetics of the coverage fraction $\theta(t) = \sigma n(t)/S$ (where n is the number of deposited particles) and the jamming limit θ_J are well known. For spherical objects we have $\theta_j - \theta(t) \propto t^{-1/d}$, where $\theta_j \approx 0.7476\ldots$ for $d = 1$ [16] and $\theta_j \approx 0.547\ldots$ for $d = 2$.

Note that d indicates the dimension of the adsorption space, meaning that our model introduces bulk diffusion on a $(d+1)$-dimensional lattice. For the case $d = 1$, our simulations were performed on a lattice of size $N_x = 2048$ and $N_z = 64$. The initial concentration was fixed in the range $\rho \in [0.1, 0.4]$, sufficently low to avoid strong correlations between depositions occurring at the same time. The diameter of the particles σ was fixed at half the lattice size. D is chosen in the range $[0.01, 0.25]$ and finally $q \in [0.25, 1]$. For each set of control parameters 100 simulations were carried out and the results were averaged.

IV. RESULTS

A. The initial regime

Clearly, the very early regime ($\tau \ll 1$) of both DA and RSA processes behaves as $\theta \propto \tau$ since every deposition at-

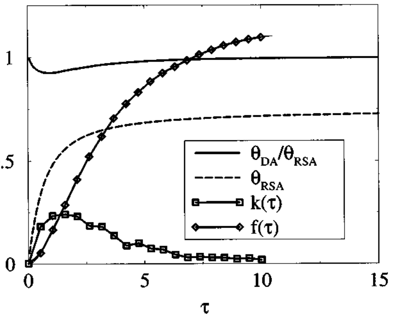

FIG. 2. Comparison between RSA and DA processes. The DA coverage was averaged over 100 simulations with the following set of parameters: $\rho=0.1$, $D=0.25$, and $q=1.0$ ($N_x=2048$, $N_y=64$, and $\sigma=0.5$). The figure shows the RSA coverage θ_{RSA}, the coverage ratio $\theta_{\mathrm{DA}}/\theta_{\mathrm{RSA}}$, $f(\tau)$, and $k(\tau)=f'$, the so-called flux of trapped particles.

tempt must be successful. Later on, but still during the initial phase, the exclusion effect of the partly covered surface slows down the process. For RSA the deposition attempts are fully uncorrelated and the following mean-field-like expression holds:

$$\frac{d\theta}{d\tau}=J\phi. \tag{3}$$

J is the rate of deposition: $J_{\mathrm{RSA}}=1$ according to the definition of τ. $\phi(\theta)$ is the fraction of surface available for deposition, for which several expansions have been given as a function of the coverage [17]. During a DA process the diffusion correlates the deposition attempts and thus invalidates the left-hand side of Eq. (3).

These correlations lead to a jamming coverage dependent on the details of the transport process. We focus on this and concomitant slight changes in the structure of the deposit in Sec. IV B. Here we assume as a first approximation that

$$\phi_{\mathrm{RSA}}(\theta)=\phi_{\mathrm{DA}}(\theta). \tag{4}$$

To first order, these correlations lead to an overestimation of J: some particles become *trapped* in growing zones of excluded surface in which all successive deposition attempts will fail. Consequently, we may rewrite Eq. (3) as

$$\frac{d\theta_{\mathrm{DA}}}{d\tau}=[1-k(\tau)]\phi(\theta_{\mathrm{DA}}). \tag{5}$$

Due to the approximation (4) a time delay $f(\tau)$ can fully take into account the difference between the two kinds of process such that

$$\theta_{\mathrm{DA}}(\tau)=\theta_{\mathrm{RSA}}(\tau-f(\tau)). \tag{6}$$

It is straightforward to determine f numerically (see Fig. 2). By substituting Eq. (6) into Eq. (5), it can be given a physical interpretation by noting that $f'=k$, the flux correction, or the flux of particles trapped as described above.

Figure 2 shows the typical evolution of k, which, independently of the simulation parameter values, starts at zero at $\tau=0$ and subsequently passes through a maximum around $\tau=1$. This is in accord with the concept of trapped particles, which must clearly appear progressively and yet are only significant in the initial regime. Later, the rate of increase of the covered surface is slow enough to allow the effective decorrelation of J.

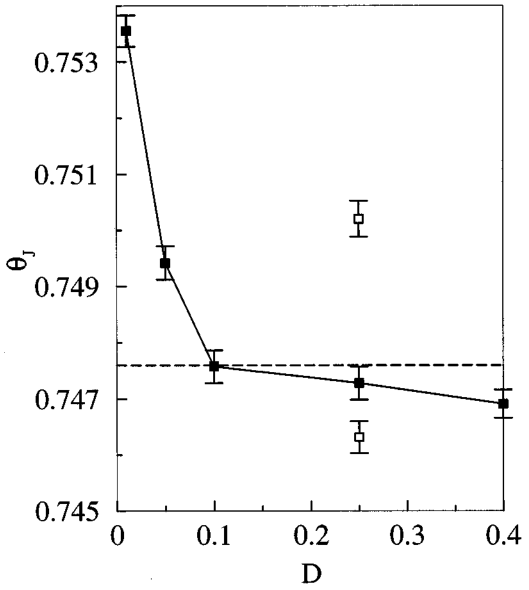

FIG. 3. Jamming coverage fraction θ_j, for $\rho=0.1$ and $q=1.0$, as a function of the diffusion coefficient of bulk particles D (in natural lattice units). The dashed line indicates the RSA jamming value for comparison. The filled squares are obtained by imposing an extra relation among the p_i's. The error bars arise from the statistical analysis over a sampling of 50 simulations. The solid line is merely to guide the eye. The empty squares correspond to two extreme choices of p_i for the case $D=1/4$, namely, $p_2 \ll 1$ for the smallest value of θ_j and $p_2 \approx 1/2$ for the highest.

The effect of the simulation parameters ρ, D, q on the magnitude of k can readily be deduced from the above arguments and is indeed confirmed by our simulations. As q decreases and D increases, DA becomes indistinguishable from RSA since the correlations are no longer important. Moreover, these two conditions as well as large ρ promote the rapid establishment of a constant flux, whereupon the distinction between t and τ becomes superfluous and an RSA-like process is observed in laboratory time.

B. The jammed state

In the preceding subsection we assumed that the jammed state was unaffected by diffusion. This is not strictly true, but the discrepancy appears to be a higher-order effect. In Fig. 3 we plot the value θ_j as a function of D. It has already been observed in [7] that θ_j may differ from the RSA value for DA processes. Here we show a more precise relation between θ_j and the kinetics of the bulk particles. Actually, we observe that θ_j depends on the details of the random walk: different choices of p_i yield different values of θ_j. It is not merely that θ_j is a function of the diffusion coefficient D since the function $D=D(p_i)$ is not one to one: due to the memory effects of the adsorption process, fine microscopic aspects of the bulk dynamics are visible in the jamming limit and even in the structure of the deposit.

More intuitively, our observations can be summarized as follows. The more efficiently the diffusing particles visit the bulk (either because of an increasing diffusion constant or a significant $\pi/2$ rotation probability or because of a bigger flux of new particles, i.e., ρ) after having been rejected by the covered surface, the less efficiently they cover the surface at jamming.

We focus now on the structure of the jammed state. As was recently shown for the RSA of dimers on a discrete one-dimensional lattice [18], there are evident traces of the arrival history in the jammed state and this provides a different framework to discriminate between RSA and DA processes: the mean averaged gap $g(t)$, defined later in Eq. (8), around adsorbed particles is a decreasing function of their age of deposition and may depend on the type of process. In order to carry out the comparison between DA and RSA processes, we first generalize Ziff's calculations [18] to the case of the continuum adsorption surface.

Let $P(x,t)$ denote the probability of finding an uncovered or empty interval of length at least x. It has been shown [2] that the identity $P(x,t)=P(1,t)\exp[-kt(x-1)]$ for $x\geqslant 1$ is consistent with the rate equation for $P(x)$. Let $G(x)$ denote the average gap at either end of an interval of length x after this gap has been filled to saturation. Clearly $G(x)=x$ for $x\in[0,1[$. For $x\geqslant 1$, $G(x)$ can be calculated piecewise: supposing we know $G(u)$ for $u\leqslant x-1$, the probability of depositing the first element at position u in the free interval of length x is $du/(x-1)$. After this deposition we are left with an interval of length $u\in[0,x-1]$ for which $G(u)$ is known by hypothesis. Thus we can write the recursive relation

$$G(x)=\begin{cases} x & \text{for} \quad x\in[0,1[\\ \displaystyle\int_0^{x-1}\frac{G(u)du}{x-1} & \text{for} \quad x\geqslant 1. \end{cases} \tag{7}$$

At time t the creation rate of gaps of length x is proportional to $P(x+1)$ so that the averaged gap $g(t)$ around particles adsorbed at time t is

$$g(t)=\frac{\displaystyle\int_0^{\infty}dx\ G(x)P(x+1)}{\displaystyle\int_0^{\infty}dx\ P(x+1)}=kt\int_0^{\infty}dx\ G(x)e^{-ktx}. \tag{8}$$

After some algebra we obtain $g(t)=1/t$ for $t\gg 1$ and $g(t\rightarrow 0)=G(\infty)$. From the above calculations, we have numerically estimated $G(\infty)=0.381\,80\ldots$.

It is thus not surprising that any structural analysis of the jammed states averaged over the entire configuration, such as the comparison of the radial distribution function in Ref. [6], may not reveal differences existing between RSA and DA processes, unless the measurement is done at finite time. As a matter of fact, because of their distinguishable kinetics, we do observe a difference between RSA and DA when measuring $g(t)$ at jamming, as illustrated in Fig. 4.

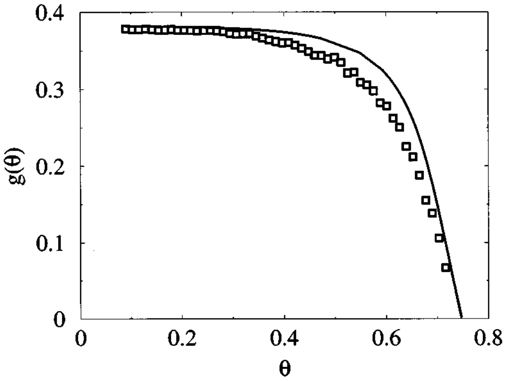

FIG. 4. Plot of the mean gap g (in units of σ) around deposited particles as a function of the coverage corresponding to the epoch of their deposition. The solid line corresponds to the RSA process and the squares represent to the DA process with the same parameters as in Fig. 2.

C. The two-dimensional case

Similar but less extensive simulations were performed for the two-dimensional case. The discrepancies between RSA and DA become less important, if not to say negligible, for the case $d=2$, because of the rapid establishment of a nearly constant overall rate of deposition and a fast homogenization (compared to the deposition time) of the bulk concentration just above the surface and thus a rate of deposition slowly varying in time and space.

V. CONCLUSION

RSA is a powerful mechanism for representing deposition of particles on a surface. Details of the transport are neglected. Nevertheless, for deposition from the solution, which is an important pratical realization of the process, omission of the diffusive mechanism bringing particles to the surface overestimates the deposition rate in the intermediate regime. The discrepancy, compared with RSA, increases as D decreases, q increases, and ρ decreases.

DA and RSA rates converge close to the jamming limit, but the limits themselves are not identical. Qualitatively this is because diffusion introduces strong lateral correlations between successive adsorption attempts. The effect is much more pronounced in one dimension than in two dimensions, because homogenization of the particle distribution in the bulk volume is more effective in the latter case.

ACKNOWLEDGMENTS

We thank the Human Frontier Science Program Organization for financial support of this work.

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[1] J. J. Ramsden, Phys. Rev. Lett. **71**, 295 (1993).
[2] J. W. Evans, Rev. Mod. Phys. **65**, 1281 (1993).
[3] I. Langmuir, J. Am. Chem. Soc. **40**, 1361 (1918).
[4] P. Schaaf, A. Johner, and J. Talbot, Phys. Rev. Lett. **66**, 1603 (1991).
[5] G. Tarjus and P. Viot, Phys. Rev. Lett. **68**, 2354 (1992). B. Senger, P. Schaaf, J.-C. Voegel, A. Johner, A. Schmitt, and J. Talbot, J. Chem. Phys. **97**, 3813 (1992).

[6] B. Senger, J. Talbot, P. Schaaf, A. Schmitt, and J.-C. Voegel, Europhys. Lett. **21**, 135 (1993).
[7] G. Doolen, *Lattice Gas Methods for Partial Differential Equations* (Addison-Wesley, New York, 1990).
[8] B. Chopard, M. Droz, and M. Kolb, J. Phys. A **21**, 250 (1989).
[9] B. Chopard, M. Droz, and M. Kolb, J. Phys. A **22**, 1609 (1989).
[10] D. Dab and J. P. Boon, *Cellular Automata and Modelling of Complex Physical Systems* (Springer-Verlag, Berlin, 1989), p. 257.
[11] B. Chopard, P. Luthi, and M. Droz, Phys. Rev. Lett. **72**, 1384 (1994).
[12] B. Chopard, P. O. Luthi, and M. Droz, J. Stat. Phys. **76**, 661 (1994).
[13] J. Bafaluy, B. Senger, J.-C. Voegle, and P. Schaaf, Phys. Rev. Lett. **70**, 623 (1993).
[14] B. Chopard and M. Droz, J. Stat. Phys. **64**, 859 (1991).
[15] A. Rényi, Publ. Math. Inst. Hung. Acad. Sci. **3**, 109 (1958).
[16] P. Schaaf and J. Talbot, J. Chem. Phys. **91**, 4401 (1989).
[17] R. M. Ziff, J. Phys. A **27**, L657 (1994).