LETTER TO THE EDITOR

An adsorption–desorption process on a line: kinetics of the approach to closest packing

X Jin†, G Tarjus‡ and J Talbot†

† School of Chemical Engineering, Purdue University, West Lafayette, IN 47907, USA
‡ Laboratoire de Physique Théorique des Liquides*, Université Pierre et Marie Curie, 4 place Jussieu 75252, Paris Cedex 05, France

Abstract. We study an adsorption–desorption process of rods on a line. The desorption rate is infinitely small, so that each desorption event is instantly followed by the insertion of one or two new rods. Due to the latter possibility, the system evolves continuously to a close-packed state. The asymptotic kinetics of the densification process is analysed with the aid of gap distribution functions. If it is assumed that the system relaxes completely to equilibrium after each density increment, we show that $1 - \rho(t) \sim 1/\ln(t)$, while an improved description yields $1 - \rho(t) \sim 1/\ln(2t(\ln 2t)^2)$. The range of validity of the asymptotic expressions is established by comparison with the results of a numerical simulation of the process.

Our understanding of irreversible adsorption processes has grown considerably during the last few years. Much of the effort has focused on the random sequential adsorption (RSA) process [1]. Some recent experimental studies have verified, at least to a degree, the predictions of this model for the adsorption kinetics of the protein transfer on oxide surfaces [2]. The simple RSA model is completely irreversible: no relaxation processes of any kind are allowed. Although, in the above example the adsorption is manifestly irreversible, in many other situations it is expected that surface diffusion and/or desorption are significant. It is clearly of interest, therefore, to extend the RSA models to incorporate these cases. Tarjus *et al* [3] considered the effect of these two mechanisms (independently) on the RSA kinetics in the low-to-intermediate density regime. More recently, Privman and Barma [4] developed a fast-diffusion mean-field approximation for the kinetics of deposition of rods on a linear substrate with diffusional relaxation.

In this letter, we examine the adsorption–desorption process of rods on a linear substrate. Hard rods adsorb randomly and sequentially at a rate k_a and desorb at a rate k_d. Unlike the simple RSA model ($k_d = 0$), it appears that analytic solutions of this model, even in 1D, are not feasible. However, one may make considerable progress for a special case of this model; namely for $k_d \to 0$, i.e. an infinitely slow desorption rate. We imagine that such a process starts at $t = 0$ on an empty line. In the initial phase of the process there is no desorption, but an infinite number of sequential adsorption attempts. The system, therefore, evolves exactly like the simple RSA process and reaches a jammed state at a density of $\theta_\infty = 0.747 \ldots$ [5]. The initial phase is followed by a succession of *desorption–adsorption events* in which one rod detaches from the surface and the resulting hole is filled by either one or two new rods. Because the latter possibility results in an increase of the number of adsorbed particles, the system evolves continuously towards a close-packed state, $\rho = 1$.

---

* Unité de Recherche Associée au CNRS (URA 765).

The rods desorb randomly, and, in particular, independently of the time over which they have been adsorbed.

To analyse the kinetics of this densification process, we introduce the following quantities. The unit of time is k_d^{-1}, or the number of desorption–adsorption events. Let $G(h, t)$ denote the density of gaps of length h, and $G(h_1, \ldots, h_n, t)$ the n-gap density such that all gaps of length $h_1, h_2, \ldots, h_n$ are ordered from left to right on the line and that any given gap in the sequence is separated from its next neighbour by one rod. Because the configurations are always jammed, $G(h, t) = 0$ for $h > 1$, and $G(h_1, \ldots, h_n, t) = 0$ if $\exists\, i \in \{1, \ldots, n\}, h_i > 1$. These density functions satisfy the following relations:

$$\int_0^\infty \mathrm{d}h\, G(h, t) = \rho(t) \qquad \int_0^\infty \mathrm{d}h\, hG(h, t) = 1 - \rho(t) \tag{1}$$

and

$$\int_0^\infty \mathrm{d}h_1\, G(h_1, \ldots, h_n, t) = \rho(t)G(h_2, \ldots, h_n, t)$$

$$\int_0^\infty \mathrm{d}h_n\, G(h_1, \ldots, h_{n-1}, h_n, t) = \rho(t)G(h_1, \ldots, h_{n-1}, t)\,. \tag{2}$$

The rate equation for $G(h, t)$ can be written as

$$\frac{\mathrm{d}}{\mathrm{d}t}G(h, t) = \left(\frac{\partial G(h, t)}{\partial t}\right)_\rho + \left(\frac{\partial G(h, t)}{\partial \rho}\right)_t \dot{\rho}(t)\,. \tag{3}$$

The first term on the right-hand side of the above equation corresponds to a relaxation at constant density, and the other to a densification mechanism. In the former, a desorbing rod is replaced with only one new rod, whatever the available space, while the latter takes into account situations in which a desorption event creates a gap of length > 2 and two new rods can be inserted instead of one. Similar rate equations can be written for higher-order gap densities. In what follows, we examine first the two mechanisms separately, but one must recall that they are coupled.

Relaxation at constant density. The kinetics in this case are described by a hierachy of equations,

$$\left(\frac{\partial G(h, t)}{\partial t}\right)_\rho = -2G(h, t) + \frac{2}{\rho}\int_h^\infty \frac{\mathrm{d}h'}{h'}\int_0^{h'} \mathrm{d}h''\, G(h'', h' - h'', t) \tag{4}$$

$$\left(\frac{\partial G(h, h', t)}{\partial t}\right)_\rho = -3G(h, h', t) + \frac{1}{h+h'}\int_0^{h+h'} \mathrm{d}h''\, G(h'', h + h' - h'', t)$$

$$+ \frac{1}{\rho}\int_{h'}^\infty \frac{\mathrm{d}h''}{h''}\int_0^{h''} \mathrm{d}h'''\, G(h, h''', h'' - h''', t)$$

$$+ \frac{1}{\rho}\int_h^\infty \frac{\mathrm{d}h''}{h''}\int_0^{h''} \mathrm{d}h'''\, G(h''', h'' - h''', h', t) \tag{5}$$

etc, which we may understand as follows. Consider, for instance, equation (4). Gaps of length h are destroyed by desorption of either one of the surrounding rods, and created by the re-insertion of rods into a larger gap. The probability that adsorption of the only additional particle in the length $h' + 1$ will create an interval of length between h and $h + \mathrm{d}h$ is $2\mathrm{d}h/h'$ and $\rho^{-1}\int_0^{h'} \mathrm{d}h''\, G(h'', h' - h'', t)$ is the density of gaps of length $h' + 1$ created by desorption of one particle. It is easy to verify by integration of (4) and use of (1) and

(2) that the zeroth and first moments of $G(h, t)$ (ρ and $1 - \rho$, respectively) are independent of time. If we totally neglect the densification mechanism, the system evolves at constant density ρ until it reaches a state corresponding to the stationary solution of the hierachy, equations (4) and (5). We find that the equilibrated state characterized by [6]

$$G^{\text{eq}}(h_1, \ldots, h_n, \rho) = G^{\text{eq}}(h_1, \rho) \ldots G^{\text{eq}}(h_n, \rho) \tag{6}$$

with

$$G^{\text{eq}}(h, \rho) = \frac{\rho^2}{1 - \rho} \exp\left(-\frac{\rho}{1 - \rho} h\right) \qquad h \geqslant 0 \tag{7}$$

is the stationary solution of the hierachy. We note that the superposition property, implied by (6), of the equilibrium configurations is *not* valid for those of the RSA process [7]. Since the destruction rates in (4) and (5) are independent of the gap lengths, one expects the approach towards equilibrium to be exponential. As a first approximation, it is indeed possible to show that the relaxation goes asymptotically as $\exp(-\frac{2}{3}t)$.

Densification mechanism. The densification kinetics for $G(h, t)$ are governed by the following equations:

$$\left(\frac{\partial G(h, t)}{\partial t}\right)_{\dot\rho} = \begin{cases} 0 & h > 2 \\ -\left(\dfrac{\partial G(h, t)}{\partial t}\right)_{\rho} = -2 \displaystyle\int_h^2 \mathrm{d}h' \dfrac{g(h', t)}{h'} & 2 > h > 1 \\ 2 \displaystyle\int_{h+1}^2 \dfrac{\mathrm{d}h'}{h' - 1} \left(\dfrac{\partial G(h', t)}{\partial t}\right)_{\rho} = 4 \displaystyle\int_{h+1}^2 \mathrm{d}h' \dfrac{g(h', t)}{h'} \ln\left(\dfrac{h' - 1}{h}\right) & 1 > h \geqslant 0 \end{cases} \tag{8}$$

where we have introduced

$$\rho(t) g(h, t) = \int_0^h \mathrm{d}h'\, G(h', h - h', t) \tag{9}$$

and the property that $G(h, t) = 0$ for $h > 1$. The above equations are derived by considering that one and only one additional rod can be inserted in the holes left vacant by the relaxation step. For such a hole of length h' (with a density $(\partial G(h', t)/\partial t)_\rho \mathrm{d}h'$), the probability that the additional particle will create a gap of length between h and $h + \mathrm{d}h$ (on the right or the left) is $2\mathrm{d}h/(h' - 1)$, if $2 \geqslant h' \geqslant h + 1$ and $h \leqslant 1$. Similar equations can be obtained for higher-order gap densities. As a result of the densification step, the density of particles increases at a rate equal to the number of holes which can accommodate an additional particle and are left after the relaxation step. Hence,

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = \int_1^2 \mathrm{d}h \left(\frac{\partial G(h, t)}{\partial t}\right)_\rho = 2 \int_1^2 \mathrm{d}h\, g(h, t) \frac{(h - 1)}{h} \tag{10}$$

where we have made use of (8). This equation also has a simple physical interpretation: the integrand represents the density of particles surrounded on the left and right by gaps of total length h times the probability that when that particle desorbs, two particles will fill the vacated space.

The full process is described by considering the net result of the relaxation and the densification steps, which gives for the gap distribution function

$$\frac{\mathrm{d}G(h, t)}{\mathrm{d}t} = G(h, t) = 0 \qquad h > 1 \tag{11}$$

$$\frac{dG(h, t)}{dt} = -2G(h, t) + 2 \int_h^2 dh' \frac{g(h', t)}{h'} + 4 \int_{h+1}^2 dh' \frac{g(h', t)}{h'} \ln\left(\frac{h'-1}{h}\right)$$
$$1 > h \geqslant 0 \tag{12}$$

together with (10). In the full process, the relaxation and the densification mechanisms are fully coupled. However, at large times and densities close to one, we expect that the relaxation step is much more efficient, and hence faster, than the densification step. This idea guides our treatment of the problem.

Zeroth-order description. We assume that the system relaxes fully to equilibrium after each successful addition. For a density ρ of adsorbed particles, the fraction of the line which is available to the centre of an additional rod is

$$\phi(\rho) = \phi^{eq}(\rho) = \int_1^\infty dh\, (h - 1)G^{eq}(h, \rho) = (1 - \rho)\exp(-\rho/(1 - \rho)) \tag{13}$$

where we have used the equilibrium distribution (7). The time evolution of the adsorbed particles is thus given by

$$\frac{d\rho}{dt} = (1 - \rho)\exp(-\rho/(1 - \rho)) \tag{14}$$

which is exactly the equation obtained by Privman and Barma in their mean-field treatment of an adsorbing system with fast diffusional relaxation [4]. The approach towards the close-packing ($\rho = 1$) configuration is slow:

$$\rho(t) \approx 1 - \frac{1}{\ln(t \ln(t))} \qquad t \gg 1. \tag{15}$$

Improved description. The actual process is slightly faster than that given by (15) since one does not have to wait for a full equilibration of the system before inserting an additional particle: as soon as any gap larger than one appears it is instantaneously filled. Therefore, in developing an improved description we require that all n-gap densities be zero at any time whenever one gap is larger than one. Furthermore, we note that for gaps smaller than one, the relaxation process is much faster than that induced by the densification process (roughly $\exp(-\frac{2}{3}t) \sim \exp(-\frac{2}{3}\exp(1/(1 - \rho)))$ and $1/\ln(t) \sim 1 - \rho$, respectively.) As a consequence of these two observations, we make the following approximation:

$$G(h, t) \approx G^{eq}(h, \rho(t)) \qquad 0 \leqslant h < 1$$
$$G(h, t) = 0 \qquad h > 1 \tag{16}$$

$$G(h, h', t) \approx G^{eq}(h, h', \rho(t)) = G^{eq}(h, \rho(t))G^{eq}(h', \rho(t)) \qquad 0 \leqslant h, h' < 1$$
$$G(h, h', t) = 0 \qquad h > 1 \text{ or } h' > 1. \tag{17}$$

From (9) and (10) we find

$$\frac{d\rho}{dt} \approx 2\exp(-\rho/(1 - \rho)). \tag{18}$$

The leading term in the asymptotic behaviour is then

$$\rho(t) \approx 1 - \frac{1}{\ln(2t(\ln 2t)^2)} \qquad t \gg 1. \tag{19}$$

In order to verify the asymptotic behaviour and establish the density at which the asymptotic behaviour begins, we have performed a numerical simulation of the adsorption–desorption process. In the first step, a jammed RSA configuration of rods was generated on an open interval of length L (in units of the rod diameter). The adsorption–desorption phase
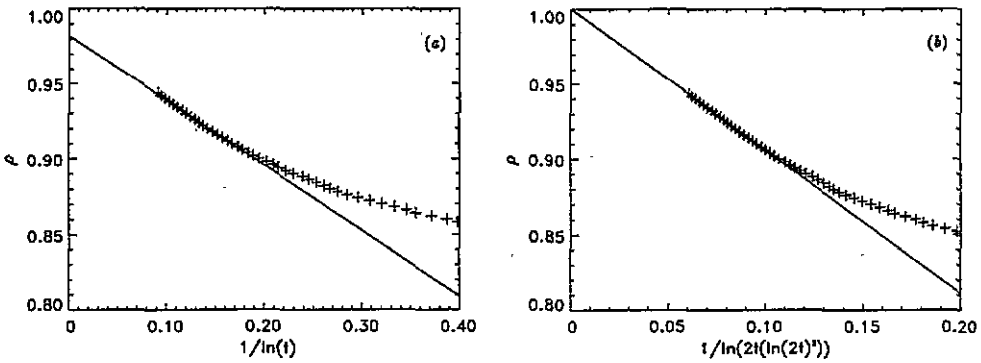
Figure 1. Simulation of the desorption–adsorption process. The simulations were performed on an open line segment of length $L = 500$ rod diameters. Each point is an average over 80 independent simulations. Plots (a) and (b) test the zeroth order and improved asymptotic kinetics, respectively.
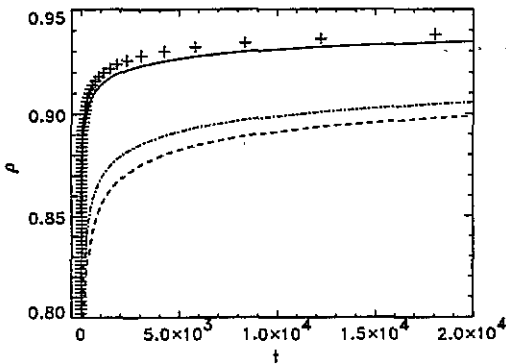

Figure 2. Density as a function of time. The simulation results ($N_{DAE} = 10^7$, $L = 500$, $N_{AV} = 80$) are shown by the symbols. The lines are, from top to bottom, $1 - 1/\ln(2t(\ln 2t)^2)$, $1 - 1/\ln(2t)$, and $1 - 1/\ln(t)$, respectively.

then begins. A randomly selected rod is removed from the surface and a new rod is inserted randomly and uniformly in the resulting gap. If, after this step, a gap of length greater than one exists to the left or right of the newly inserted particle, a second rod is randomly placed to fill this gap. The unit of time is defined as $t = N_{DAE}/L$, where N_{DAE} denotes the number of adsorption–desorption events. A number of independent runs are performed to obtain good statistics. The results shown in figure 1 confirm the analysis presented above. A plot of ρ versus $1/\ln(t)$ displays a linear region above a density of about 0.91. A least-squares fit of the data for $0.907 < \rho < 0.948$ yields an intercept of 0.982 and slope -0.43. A similar plot, but with the abscissa replaced with $1/\ln(2t(\ln(2t))^2)$, shows that (19) does indeed have a larger range of validity: the linear region persists to lower densities, and a least-squares fit of the data for the same range of density as above has an intercept of 1.0005 and slope of -0.947. The greater accuracy of (19) is even more dramatically illustrated in figure 2 which shows ρ versus t. This excellent agreement confirms that the adsorption–desorption process with vanishingly small desorption approaches close packing with a slow logarithmic behaviour similar to that predicted for an adsorption with very fast diffusional relaxation. It also suggests that (16) and (17) represent a good description of

the gap densities even when the system is 10% below close packing.

Acknowledgments

References

[1] Evans J W 1993 *Rev. Mod. Phys.* **65** 1281
[2] Ramsden J 1993 *Phys. Rev. Lett.* **71** 295
[3] Tarjus G, Schaaf P and Talbot J 1990 *J. Chem. Phys.* **93** 8352
[4] Privman V and Barma M 1992 *J. Chem. Phys.* **97** 6714
[5] Rényi A 1963 *Sel. Trans. Math. Stat. Prob.* **4** 205
[6] Meeron E A and Siegert A J F 1968 *J. Chem. Phys.* **48** 3139
[7] This can be shown using the results of Viot P, Tarjus G, and Talbot J 1993 *Phys. Rev. E* **48** 480 in the limit $a = 0$
[8] P L Krapivsky and E Ben-Naim *Preprint*