Dissociative Adsorption: A Solvable Model

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Abstract: A model of "hot"-dimer deposition in one dimension, introduced by Pereyra and Albano, is modified to have an unbounded dissociation range. The resulting dynamical equations are solved exactly. A related k-mer dissociation model is also introduced and its solution obtained as a quadrature.

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Recent experimental studies [1] reported deposition processes in which prior to adhesion the arriving diatomic molecules break up into single-atom fragments which dissipate the excess energy by "flying apart" a large distance. A simplified one-dimensional (1D) model of these processes was introduced in [2]. The restriction to 1D was motivated by the possibility of extensive numerical Monte Carlo studies, and in fact, more realistic two-dimensional-substrate Monte Carlo modeling was alluded to in [2]. It is usually instructive to obtain solvable variants of 1D models. Indeed, exact calculations provide insight into more realistic higher-dimensional systems and yield test models for approximation schemes, in various reaction and adsorption processes reviewed, e.g., in [3-6].

In this work, we introduce a model with infinite dissociation range and with random initial conditions, which can be solved exactly for dimers as well as generalized to k-mer deposition with dissociation. The latter generalization allows discussion of the approach to the continuum limit [7-8].

In the deposition of "hot" dimers [2], one assumes that each successful deposition attempt in followed up by the dissociation of the dimer. The two monomer fragments move apart up to a certain maximal distance: they either stop on their own or run into existing clusters. In order to eliminate the upper bound on the allowed dissociation distance while still have the resulting model not sensitive to the finite-size end-effects, one has to consider initial states in which obstacles to the motion of the fragments after deposition are present with reasonable density. Thus we assume that initially the lattice is randomly covered with some finite monomer density ρ, measured per lattice site.

Each dimer deposition event will be followed by instantaneous fragmentation and attachment of one monomer fragment at each end of the empty gap in which the deposition attempt has succeeded. Thus the gap size will be decreased by 2. For k-mer deposition, with $k = 3, 4, 5, \ldots$, the way in which the k-mer breaks down into two fragments is irrelevant as far as the effect of the deposition event on the gap length is concerned. Indeed, the gap will be shortened by k sites no matter in what proportion were the original k monomers placed at each of its ends. Monomer deposition, $k = 1$, can be also treated, with obvious modifications.

The exact solvability of the resulting model is then nearly obvious. The gap sizes evolve independently, unlike in models with finite dissociation range [2] and in related models [9] where the relaxation is by diffusion. The fact that added deposition processes confined to the gap ends do not impede exact solvability has also been noted in random sequential adsorption with "ballistic relaxation" [10].

It is convenient to consider a lattice of N sites, although we will disregard any end effects (i.e., the limit $N \to \infty$ will be always assumed). Let $P_m(t)N$ denote the number of gaps exactly m empty sites long, at time t. The initial random distribution corresponds to

$$P_m(0) = \rho^2 (1-\rho)^m \ , \tag{1}$$

where $m = 0, 1, 2, \ldots$. The coverage fraction, $\theta(t)$, is initially $\theta(0) = \rho$.

We assume that the deposition attempts are random and uncorrelated at various lattice sites, with the rate R per site. Note that for an N-site lattice there are N distinct k-mer deposition locations (if we disregard end effects). The rate R is defined per each lattice location, and it will be conveniently absorbed in the definition of the dimensionless time variable,

$$\tau = Rt \ . \tag{2}$$

Of course, only deposition attempts for which the k-mer fully fits in an empty gap are successful. Other attempts are rejected.

Since the fragments of the dissociation are transported to the ends of the gaps, the time evolution of the gap numbers satisfies a simple set of relations,

$$\frac{dP_m}{d\tau} = -(m-k+1)P_m + (m+1)P_{m+k} \qquad \text{for} \qquad m \geq k-1 \ , \tag{3}$$

$$\frac{dP_m}{d\tau} = (m+1)P_{m+k} \qquad \text{for} \qquad 1 \leq m \leq k-1 \ . \tag{4}$$

The relations (3) can be solved in closed form by standard methods such as generating functions or other techniques developed for random sequential adsorption [5-6]. We only quote the result,

$$P_{m \geq k-1}(\tau) = \frac{\rho^2 (1-\rho)^m e^{-(m-k+1)\tau}}{\left[1-(1-\rho)^k \left(1-e^{-k\tau}\right)\right]^{(m+1)/k}} \ . \tag{5}$$

The coverage can be obtained by summing up the monomer deposition rates in the $m \geq k$ gaps,

$$\frac{d\theta}{d\tau} = k \sum_{m=k}^{\infty} (m - k + 1) P_m \ . \tag{6}$$

This relation leads to a quadrature which could not be evaluated in closed form for general k; see (12) below. Similarly evaluation of the gap numbers for $1 \leq m \leq k - 1$ requires integration (for $k > 2$); see (4). Thus, an alternative expression for the coverage via the fraction of unoccupied sites,

$$1 - \theta = \sum_{m=1}^{\infty} m P_m \ , \tag{7}$$

still involves quadratures for general k.

We are particularly interested in the cases $k = 1, 2$ and $k \to \infty$. Fortunately, for all these values of k further progress is possible. We report the results for each case in turn. First, consider the monomer deposition process which is expected to proceed to full coverage at large times. Indeed, the exact expression is simply

$$\theta_{k=1}(\tau) = 1 - (1 - \rho) e^{-\tau} \ . \tag{8}$$

Calculation of the coverage for the dimer deposition, $k = 2$, is also straightforward. Indeed, all the terms needed in (7) are given by the solution (5) (which is no longer the case for $k > 2$). The resulting expression,

$$\theta_{k=2}(\tau) = 1 - \frac{1-\rho}{(2-\rho)^2} \left[(2-\rho)\rho + 2(1-\rho)^2 e^{-2\tau} + 2(1-\rho) e^{-\tau} \sqrt{1 - (1-\rho)^2 \left(1 - e^{-2\tau}\right)} \right] \ , \tag{9}$$

was also checked by calculating (6).

Since each gap shrinks independently of all other gaps in this model, the evolution of the gap size distribution could also be studied in terms of the probability distribution of stochastic gap-size variables $m(t)$ decreasing in steps of k at the rates proportional to $m(t) - k + 1$ for $m(t) \geq k$, and zero for $0 \leq m(t) < k$. The value $m(0)$ can be considered fixed for computational purposes, and the final expressions averaged over the initial m-value distribution (1). For finite times this approach does not seem to yield new useful results. However, for time $t = \infty$ all $m(0)$-size gaps will be reduced mod(k) to the values $m(\infty) = 0, 1, \ldots, k - 1$. Therefore the $t = \infty$ "jamming" coverage can be calculated as

$$\theta(\infty) = 1 - \sum_{m=1}^{k-1} m \sum_{j=0}^{\infty} P_{m+jk}(0) = \rho \left[1 + \frac{k(1-\rho)^k}{1 - (1-\rho)^k} \right] \ . \tag{10}$$

The $\tau = \infty$ values for $k = 1, 2$ are consistent with (8) and (9). Note that the limiting coverage for $k = 2$ is less than 1, and it depends on the initial density ρ via

$$\theta_{k=2}(\infty) = \frac{1 + (1-\rho)^2}{2-\rho} \ . \tag{11}$$

An interesting property of the jamming coverages (10) is that they are nonmonotonic functions of ρ for $0 < \rho \leq 1$. The rate of approach to the jamming limit is $\sim e^{-\tau}$.

We now turn to the general-k relation (6) which can be reduced to the form

$$\frac{d\theta}{d\tau} = \frac{k\rho^2 (1-\rho)^k e^{-\tau}}{\left[1 - (1-\rho)^k \left(1 - e^{-k\tau}\right)\right]^{(k-1)/k}} \left\{ \left[1 - (1-\rho)^k \left(1 - e^{-k\tau}\right)\right]^{1/k} - (1-\rho) e^{-\tau} \right\}^{-2} \ . \tag{12}$$

In order to formulate the continuum limit as $k \to \infty$, similar to the procedure described for random sequential adsorption in [7-8], we define the 1D lattice with spacing decreasing as $\sim \frac{1}{k}$. The depositing k-mer objects then have fixed length. In order to keep their deposition attempt rate fixed per unit length which for $k \to \infty$ accommodates $\mathrm{O}(k)$ lattice sites, we define the deposition rate per site, R, to be proportional to $1/k$. Then the time variable finite in the continuum limit is [7-8]

$$T = k\tau \ . \tag{13}$$

The present problem, however, has a new interesting aspect in the continuum limit, not discussed in connection with random sequential adsorption studied in [7-8]. Indeed the initial conditions of placing monomers randomly with density ρ per site, correspond to the average length of empty gaps equal $1/\rho$ lattice spacings as can be easily verified from (1). Thus for ρ fixed the deposition process is blocked in the limit $k \to \infty$, i.e., the coverage remains ρ, in fact, for times $\tau < \mathrm{O}(k)$. This property is also related to the fact that the jamming coverages (10) approach asymptotically the curve $\theta(\infty) = \rho$ when the $k \to \infty$ limit is taken for fixed $\rho > 0$. To have a nontrivial limit, one has to take ρ of order $1/k$. This corresponds to vanishing initial coverage but to finite density of zero-length "obstacles" that stop the depositing object fragments upon dissociation. We take

$$\rho = \frac{1}{Mk} \ , \tag{14}$$

corresponding to the average distance of Mk lattice spacings between these "obstacles" which serve as seeds for the occupied-area "clusters" formed at finite times T.

The limiting form of (12) as $k \to \infty$ is

$$\frac{d\theta_{k=\infty}}{dT} = \frac{1}{M^2 \left(e^{1/M} - 1 + e^{-T}\right) \left[T + \ln\left(e^{1/M} - 1 + e^{-T}\right)\right]^2} \ , \tag{15}$$

while the jamming coverage (10) reduces to

$$\theta_{k=\infty}(\infty) = \frac{1}{M\left(e^{1/M}-1\right)} \; . \tag{16}$$

Thus the deposition process develops the power-law tail,

$$\theta_{k=\infty}(\infty) - \theta_{k=\infty}(T) \simeq \frac{1}{M^2\left(e^{1/M}-1\right)T} \qquad \text{for} \qquad T \gg 1 \; . \tag{17}$$

This power-law behavior is similar to the ordinary random sequential adsorption [7-8]: the tail is due to gaps arbitrary close in size to that of the depositing objects. These gaps are reached with small probability by uniformly distributed deposition attempts. For short times the continuum-limit coverage behaves according to

$$\theta_{k=\infty}(T) \simeq e^{1/M}T \qquad \text{for} \qquad T \ll 1 \; . \tag{18}$$

Finally, we point out that the $\rho \to 0$ limit of the coverage exists and is well defined for all $k = 1, 2, 3, \ldots, \infty$. The result corresponds to uncorrelated deposition of k-mers,

$$\theta_{\rho\to 0}(\tau) = 1 - e^{-k\tau} = 1 - e^{-T} \; . \tag{19}$$

This expression follows by taking the $\rho \to 0$ limit in (8), (9), (12), or the $M \to \infty$ limit in (15).

In summary, we introduced a variant of the 1D dissociative adsorption process which allows exact solution for dimers as well as derivation of various other results notably the form of the continuum behavior for limiting off-lattice deposition. The results for the time dependence of the coverage generally resemble those for random sequential adsorption [5-8]. A new feature is the form of the initial conditions required for the existence of the continuum limit.

REFERENCES

[1] H. Brune, J. Wintterlin, R.J. Behm and G. Ertl, Phys. Rev. Lett. **68**, 624 (1992).

[2] V.D. Pereyra and E.V. Albano, *Random Sequential Adsorption of "Hot" Dimers on One Dimension*, J. Phys. A, in print (1993).

[3] T. Liggett, *Interacting Particle Systems* (Springer-Verlag, New York, 1985).

[4] V. Kuzovkov and E. Kotomin, Rep. Prog. Phys. **51**, 1479 (1988).

[5] M.C. Bartelt and V. Privman, Int. J. Mod. Phys. B**5**, 2883 (1991).

[6] J.W. Evans, *Random and Cooperative Sequential Adsorption*, Rev. Mod. Phys., in print (1993).

[7] J.J. Gonzalez, P.C. Hemmer and J.S. Høye, Chem. Phys. **3**, 228 (1974).

[8] V. Privman, J.–S. Wang and P. Nielaba, Phys. Rev. B**43**, 3366 (1991).

[9] M.C. Bartelt and J.W. Evans, Phys. Rev. B**46**, 12675 (1992).

[10] J. Talbot and S.M. Ricci, Phys. Rev. Lett. **68**, 958 (1992).