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Kinetics of irreversible adsorption of mixtures of pointlike and fixed-size particles: Exact results

M. C. Bartelt
Department of Physics, Clarkson University, Potsdam, New York 13699-5820

V. Privman
Department of Physics, Clarkson University, Potsdam, New York 13699-5820
and Höchstleistungsrechenzentrum, Kernforschungsanlage Jülich GmbH, Postfach 1913, D-5170 Jülich 1,
Federal Republic of Germany

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An exact solution is reported for the kinetics of random sequential adsorption of mixtures of monomers and k-mers on a one-dimensional lattice. The limit $k \rightarrow \infty$ can then be appropriately defined, yielding the solution for the continuum deposition of a mixture of fixed-size and pointlike particles. The addition of the pointlike particles is found to modify in a nonuniversal way the form of the large-time convergence law of the approach to the jamming coverage.

Recently, there has been a renewal of interest in, and much theoretical effort devoted to, random sequential deposition processes [1–25]. Such processes are realized in experimental studies of kinetics of protein and colloid particle adhesion on surfaces under the conditions of negligibly slow surface relaxation (e.g., diffusion) [26–33].

Experimentally, it is also possible to study surface deposition kinetics of well-defined *mixtures* of different types of particles. However, there has been very little progress made in the theoretical description of such mixture-deposition processes. Most results available to date were obtained numerically or within approximation schemes [15,34–37] and no systematic theoretical picture has emerged.

In this work we establish that exact results can be obtained for a class of monolayer mixture-deposition models in one dimension (1D). Generally, the 1D deposition processes are not just of theoretical interest but they are appropriate for the description of certain polymer reactions [1,3,38–45]. To our knowledge, the only previous study on the 1D deposition of mixtures [34–36,45] was mathematically oriented and focused on the estimation of jamming coverages. We report results for the kinetics (i.e., the time dependence of the coverage) which, hopefully, will provide a useful guide for studies of the 2D deposition processes as well.

The outline of the rest of this work is as follows. First, we define the models and develop a rate-equation approach that allows derivation of exact results in many cases. We then present explicit results for the case of the deposition of mixtures of fixed-length and pointlike "particles" on 1D line "surfaces." The choice of this particular type of mixture is motivated by a recent study [37] suggesting that interesting effects are to be expected when particle sizes differ significantly. Our models are those of lattice deposition, and "pointlike" particles are defined by the appropriate continuum limit. Indeed, new interesting properties of the deposition kinetics emerge in the continuum deposition case.

For the continuum deposition of one type of particles (segments) of length l, on a 1D line, with the attempt rate R per unit length and time, it is convenient to introduce the corresponding lattice model of k-mer deposition [23]. Thus, we introduce a lattice of spacing $b = l/k$, and allow deposition only at sites where the incoming particle will coincide exactly with the underlying lattice, covering k units. The deposition frequency per site will be Rb. *Random sequential adsorption* for the lattice or continuum models is defined by assuming that the deposition attempts are successful if the incoming particles do not overlap any particles already in the deposit. Otherwise, the attempt is rejected. Thus, particles are assumed transported to the surface, but they adhere only if there is unoccupied area to fit that particle in. (We consider only monolayer deposition in this work.)

For all $k \geq 2$, the deposition process ends in a jammed state of density smaller than the close packing value, 1. The jamming coverage (density) is approached at the rate $\exp(-Rlt/k)$, for large times, t. In the limit $k \rightarrow \infty$ $(b \rightarrow 0)$ this behavior crosses over to a slower, power-law approach, $\sim t^{-1}$. These large time and many other properties of the 1D deposition have been obtained by exact calculations, and analyzed extensively [1-3,5,7,8,23]. One of the several known methods to calculate the time-dependent coverage [3,24] is particularly well suited for the extension to the case of the deposition of mixtures. In this approach one considers the probabilities $P_m(t), m = 1,2,\ldots$, that groups of m sites are not covered by particles. These groups of m consecutive sites may or may not be bound by occupied sites at one or both ends. For the one-type (k-mer) deposition problem, one can write down the exact rate equations,

$$-k\frac{dP_m}{dT} = \begin{cases} (k-m+1)P_k + 2\sum_{j=1}^{m-1} P_{k+j}, & m \leq k \quad (1) \\ (m-k+1)P_m + 2\sum_{j=1}^{k-1} P_{m+j}, & m \geq k \quad (2) \end{cases}$$

where we introduced the dimensionless time variable $T \equiv Rlt$. The first terms in (1) and (2) correspond to the k-mer covering fully the m-group $(m \leq k)$ or fitting within it $(m \geq k)$. The sums correspond to the probabilities of deposition events in which the m-group is made occupied by a partial overlap by the incoming k-mer. (The sum over j is not present for $m=1$.) Such rate equations are exact in 1D, and allow a solution in quadratures. The coverage (density of occupied sites) is given by

$$\Theta(t) = 1 - P_1(t). \tag{3}$$

An important observation is that this general setup is not affected if the deposition of mixtures is considered. Indeed, for mixtures, i.e., for the deposition of particles of different size and rate values, the rate equations for the probabilities P_m will still be linear in P_m, and of the form (1) and (2). The only changes will be: (i) more terms on the right-hand sides, with coefficients involving various rate ratios; (ii) there may be more types of equations, because there will be more particle sizes to compare (to m).

In this work we consider in detail the deposition of the mixtures of k-mers and monomers (of length b). We first present the exact solution for $\Theta(T)$ and then analyze it in the limit $k \rightarrow \infty$, when monomers become pointlike. For fixed $k \geq 2$, let $f(k)$ denote the deposition attempt frequency (per site) of monomers. We will keep the k-mer notation as before: rate R, size l, lattice spacing $b = l/k$, and dimensionless time defined by $T = Rlt$. The rate equations appropriate for this problem are then obtained by adding the term $(kf/Rl)mP_m$ to the right-hand sides of both (1) and (2). For instance, the equations for $m \geq k$ then read

$$-k\frac{dP_m}{dT} = (m-k+1)P_m + 2\sum_{j=1}^{k-1} P_{m+j} + amP_m, \qquad m \geq k \tag{4}$$

where we introduce the notation

$$a \equiv \frac{kf}{Rl}. \tag{5}$$

The resulting rate equations are supplemented by the initial conditions $P_m(0) = 1$ (for all m). The $m \geq k$ equations are then solved by the *ansatz*

$$P_{m \geq k}(T) = p(T)\exp[-m(1+a)T/k]. \tag{6}$$

The result for $p(T)$ is

$$p = \exp\left[\frac{k-1}{k}T + \frac{2}{1+a}\sum_{j=1}^{k-1}\frac{1-\exp[-j(1+a)T/k]}{j}\right]. \tag{7}$$

Next we note that the equation for P_1 only involves P_k. Explicitly, this equation is

$$-k\frac{dP_1}{dT} = kP_k + aP_1. \tag{8}$$

The expression for the coverage can therefore be obtained in closed form, by using (3),

$$\Theta = 1 - e^{-aT/k}\left[1 - \frac{1}{1+a}\int_0^{k(1-e^{-(1+a)T/k})} du \left(1-\frac{u}{k}\right)^{(k-2)a/(1+a)} \exp\left(-\frac{2}{1+a}\int_0^u dv\,\frac{1-(1-v/k)^{k-1}}{v}\right)\right]. \tag{9}$$

Note that the derivation of this result involved several rather cumbersome algebraic manipulations which are not detailed here. The form given is convenient for the large-k analysis. For small-k values, simpler expressions can be obtained by evaluating the v integral in (9).

Let us point out that the rate ratio a, defined in (5), is generally a function of k, via the k dependence of f. Some of the implications of the result (9) can be seen without the precise specification of this k dependence. For instance, one can easily see that the value $\Theta(t=\infty)$ changes discontinuously from 1 for all positive f, to the jammed-state value $\Theta(t=\infty; f=0; k) < 1$ for $f \equiv 0$. The latter values were studied, e.g., in Ref. 5. (We always assume that $R > 0$.) Indeed, when the monomer deposition frequency f is nonzero, they will eventually cover all the lattice sites. A more detailed analysis of the result (9) requires the consideration of the proper k dependence of $f(k)$. We restrict our attention to the limit $k \rightarrow \infty$ in which the lattice monomers become pointlike whereas the k-mer deposition becomes continuous, with the fixed value, l, of particle length.

If the monomer deposition rate f were allowed to stay constant as $k \rightarrow \infty$, then the monomers would completely preclude the deposition of extended particles. Indeed, one can easily see that (9) reduces to

$$\Theta(t) = 1 - e^{-ft}\left[1 - \frac{Rl}{fk} + O\left(\frac{1}{k^2}\right)\right] \tag{10}$$

in this limit. Here we restored the original time, t, and other variables to emphasize that the leading order result is just that of monomer deposition (uncorrelated growth of the coverage). This at first sight surprising conclusion has, in fact, a simple explanation. The *space-filling* capacity of the monomers decreases as $b = l/k$ (in the limit $k \rightarrow \infty$). However, their *jamming* capacity (effective only in blocking k-mer deposition) grows $\sim kb$. Indeed, a monomer excludes length l for the centers of extended particles to land (while each extended particle excludes twice that length in 1D). Keeping f fixed corresponds to increasing the monomer deposition attempt rate, $f/b = kf/l$, to keep their space-filling effect fixed. It turns out that the fixed-size (l) particles then do not play any role in the deposition process (for large k).

The above considerations suggest that a more interesting deposition process is obtained if the "pointlike particle" limit is defined with the monomer deposition frequency per site decreasing $\sim 1/k$ as $k \rightarrow \infty$. Effectively, we then keep a fixed, of order 1, in (5), and we define $f(k) = Rla/k$. The jamming ability of monomers is thus finite. Therefore, for times $T \ll k$, a nontrivial configuration will build up, by the mixture of extended and pointlike particles, with only the former contributing to the coverage density, but with both types of particles playing a role in the jamming-associated correlations affecting the kinetics of the process. The precise behavior of the coverage will depend on the rate ratio a. In fact, in this regime the coverage follows a definite limiting law,

$$\Theta(T \ll k) \simeq \Theta(T) \equiv \frac{1}{1+a}\int_0^{(1+a)T} du \exp\left[-\frac{ua}{1+a} - \frac{2}{1+a}\int_0^u dv \frac{1-e^{-v}}{v}\right]. \tag{11}$$

This expression follows from (9), up to corrections of order $1/k$.

It is interesting to note that this "intermediate" coverage reaches jamming for $T \gg 1$. The function $\Theta(T)$ is shown in Fig. 1 for several a values. The jamming values $\Theta(\infty)$ are given in Fig. 2. Naturally, both the time-dependent coverage and the jamming values decrease as a increases because the monomer contribution to the coverage is negligibly small. Note that for $a = 0$, (9) and (11) give, respectively, the previously known exact results [5] for the discrete (lattice) and continuum deposition kinetics.

Thus, the deposition process proceeds on two distinct time scales. For $T \ll k$, the coverage builds up at times T of order 1 and reaches saturation at $\theta \simeq \Theta(\infty)$ for $1 \ll T \ll k$. The deposition then continues, by monomers only, with further buildup of the coverage on the time scales of order k. Indeed, relation (9) gives, for $T \gg 1$ but no longer bounded by k from above,

$$\Theta(t) \simeq 1 - e^{-Rlat/k}[1 - \Theta(\infty)], \tag{12}$$

where we restored the original time, t. Indeed, on the time scales of order k, the monomers fill up the remaining void length, fraction $[1 - \Theta(\infty)]$, while the k-mer deposition is fully jammed.

Many authors [2,6–9,15,17,22,23,26] devoted significant effort to the studies of the large-time asymptotic behavior of the difference $\Theta(\infty) - \Theta(t)$. Indeed, the asymp-

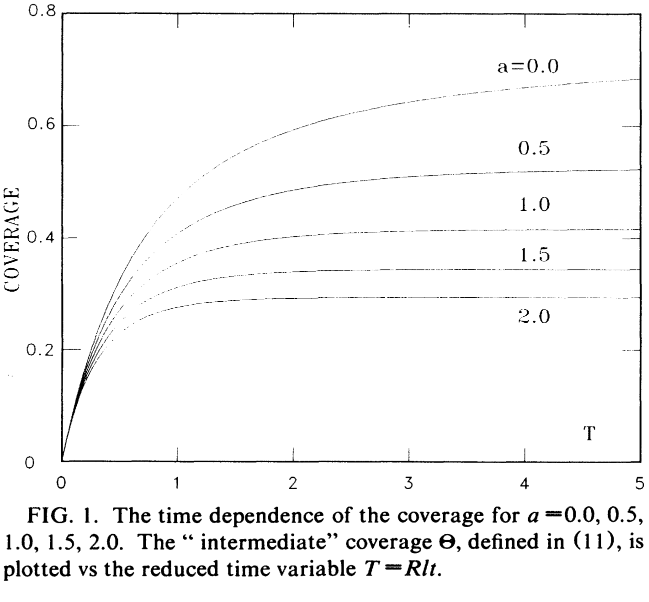

FIG. 1. The time dependence of the coverage for $a = 0.0$, 0.5, 1.0, 1.5, 2.0. The " intermediate" coverage Θ, defined in (11), is plotted vs the reduced time variable $T = Rlt$.

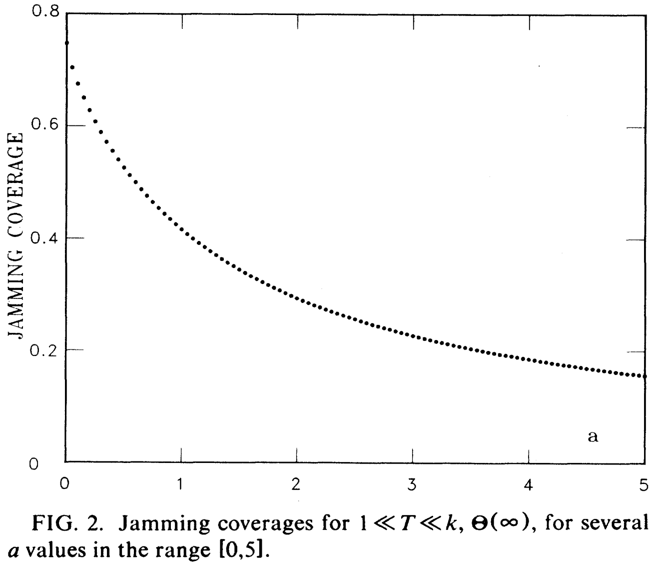

FIG. 2. Jamming coverages for $1 \ll T \ll k$, $\Theta(\infty)$, for several a values in the range [0,5].

totic convergence to the jamming value *in continuum deposition models* is power law, with possible logarithmic factors. The form of the convergence law is rather universal and depends on the dimensionality, orientational freedom, and shape of the depositing objects. In the 1D deposition, the result is the t^{-1} convergence. Generally, in the continuum deposition case the power-law behavior results from the distribution of voids which fit nearly precisely the particle shape thus making the probability of the appropriate deposition attempt vanishingly small, see Refs. [7,8,23] for details.

For the mixture considered in this work, the contribution of pointlike particles makes the standard argument inapplicable in the regime in which the k-mer deposition reaches jamming. Indeed, this regime is described by (11), a direct analysis of which yields, for $T \gg 1$,

$$\frac{d\Theta}{dT} \simeq [e^{E}(1+a)T]^{-2/(1+a)} e^{-aT} , \qquad (13)$$

where E is the Euler's constant. This relation integrates to the asymptotic convergence rate $\sim T^{-1}$ for $a=0$. However, for fixed $a > 0$ one gets the leading contribution of a different form,

$$\Theta(\infty) - \Theta(T) \simeq \frac{e^{-aT}}{a[e^{E}(1+a)T]^{2/(1+a)}} . \qquad (14)$$

This nonuniversal asymptotic behavior is due to the fact that the pointlike particles can "jam" with rate of order 1 those narrow gaps of size $l+\delta l$ which are reached only with probability of order $\delta l/l$ by the fixed-size particles.

In summary, we obtained an exact solution for the coverage of the deposition processes of k-mers and monomers on a 1D lattice. The large-k limit reveals interesting properties in the deposition of mixtures of pointlike and fixed-length particles, such as the existence of the jammed state, and the nonuniversal convergence law to the jamming coverage.

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