## **Kinetics of Random Sequential Adsorption**

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We present the first kinetic analysis specifically applicable to the random sequential adsorption (RSA) process in the intermediate coverage range. Our method is applied to hard disks adsorbing on a flat, uniform surface. Exact analytic expressions are derived for the first three coefficients of a power series for the rate of adsorption as a function of the coverage  $\Theta$ . Comparison with computer simulations shows that the third-order expansion describes the RSA process to an accuracy of better than 1% up to a coverage of 30%, i.e., up to 55% of the known jamming limit.

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The adsorption of proteins and latexes on solid surfaces is often an irreversible process<sup>1</sup> which can be described as a random sequential adsorption (RSA).<sup>2,3</sup> In this process one attempts to place immobile objects at random on a surface such that they do not overlap. Because of the condition of immobility, RSA configurations differ from their equilibrium counterparts.

Several authors have derived, for a one-dimensional RSA, an analytic expression for the coverage versus time.<sup>4,5</sup> In two or more dimensions, the asymptotic form of the adsorption rate<sup>6,7</sup> and the magnitude of the coverage in the jamming limit<sup>8</sup> (54.7% in two dimensions for disks) have been determined. The only analysis of the RSA process at low to intermediate coverages is due to Widom<sup>4</sup> who showed that in the expression for the adsorption rate in powers of the coverage  $\theta$  the coefficients of terms up to  $\theta^2$  are related to the virial coefficients of an equilibrium system. His argument, based on the potential distribution method,<sup>9,10</sup> gives no clue to the calculation of higher-order coefficients. This basic result has remained largely unnoticed so that crude Langmuir models are still used<sup>11-13</sup> to describe adsorption experiments involving proteins or other particles on solid surfaces. We emphasize that no kinetic theory specifically applicable to the RSA process in the intermediate coverage range for two or higher dimensions has been proposed. In this Letter we present a new method, based on simple geometrical and statistical considerations, which allows the exact evaluation of terms up to order  $\theta^3$ . We also compare the results with computer simulation. The expansion of the adsorption rate up to the  $\theta^3$  term describes the process with an accuracy of 1% up to a coverage of about 30%.

For convenience, we treat the case of hard disks adsorbing on a flat, uniform surface of area which we set to unity. Each disk of diameter  $\sigma$  has an exclusion circle of area  $q_1$  ( $=\pi\sigma^2$ ) devoid of the centers of other disks. Two disks form a pair if their exclusion circles overlap. A pair separated by a distance r ( $\sigma < r < 2\sigma$ ) excludes an area  $q_2(r)$  which is less than twice the single-particle excluded area  $q_1$  by an amount  $A_2(r) = 2q_1 - q_2(r)$ .  $A_2(r)$  is the area common to the two exclusion circles.

In general,  $dN/dt = K\phi$  where N is the number of adsorbed particles at time t and  $\phi$  is the average fraction of the surface available to the center of a new disk. Without loss of generality we set K=1.

It can be shown that

$$\phi = 1 - S_1 + S_2 - S_3 + S_4 - \dots, \tag{1}$$

where  $S_1 = Nq_1$ , and for n > 1

175

where  $A_n(\mathbf{r}_1, \ldots, \mathbf{r}_n)$  is the area common to the exclusion circles of *n* particles adsorbed at the positions defined by the vectors  $\mathbf{r}_1, \ldots, \mathbf{r}_n$  and  $\rho^{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n)$  is the so-called generic distribution function.<sup>14</sup>  $\rho^{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n) d\mathbf{r}_1 \ldots d\mathbf{r}_n$  represents the probability that a particle will be found in the element of surface  $d\mathbf{r}_1$  at  $\mathbf{r}_1$ , a second in  $d\mathbf{r}_2$  at  $\mathbf{r}_2$ , etc. We will not elaborate on the proof of (1) here, but only note that each new term corrects for the over counting in the previous ones [e.g., for pairs, recall that  $A_2(\mathbf{r}_1, \mathbf{r}_2) = 2q_1 - q_2(|\mathbf{r}_1 - \mathbf{r}_2|)$ ]. The proof can be found in the earliest paper on scaled particle theory, <sup>15</sup> where it applies to hard spheres and re-

 $S_n = \frac{1}{n!} \int \int \cdots \int A_n(\mathbf{r}_1, \ldots, \mathbf{r}_n) \rho^{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n) d\mathbf{r}_1 \cdots d\mathbf{r}_n,$ 

versible equilibrium configurations. However, since the proof involves only geometrical arguments, it applies to both the RSA as well as the equilibrium case. Note that for disks of only one size, terms beyond  $S_5$  do not contribute because the geometrical factors  $A_n$ , n > 5 are necessarily zero.

If we denote by  $N_2(r) dr$  the number of pairs per unit surface characterized by a center to center distance between r and r+dr,  $S_2$  can also be written in the form:

$$S_2 = \int_0^\infty A_2(r) N_2(r) \, dr \,. \tag{3}$$

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It turns out that this expression is more convenient for the calculation of  $S_2$ . For RSA,  $N_2(r)$  can be determined, up to a certain order in N, from the probability that a new particle forms a pair of separation r with one of the N particles already adsorbed. To see how this may be accomplished, consider a particular particle, previously adsorbed and place the origin of a polar coordinate system  $(r, \theta)$  at its center. For a newly adsorbed particle to form a pair with this previous one its center must lie in the interval  $\sigma < r < 2\sigma$  so that the two exclusion circles will overlap. Suppose its center is to be placed in the element of area  $r dr d\theta$ . For this to be possible there must be room for its exclusion circle, i.e., there must be a circular region (with center at  $r dr d\theta$ ), of at least radius  $\sigma$ , devoid of the centers of other disks. The probabilities for this is given by

$$p_0 = 1 - p_1 - p_2 - \cdots, (4)$$

where  $p_1$  is the chance that *exactly one* disk center is in the designated region and  $p_2$  is the chance that *exactly two* centers are in the region, etc.

Consider  $p_1$ . We are assured that the center of the one disk cannot lie in the region of mutual overlap of the two exclusion circles since the exclusion due to the previously adsorbed disk forbids it. This leaves only the area  $q_1 - A_2(r)$  for its possible location. But it could lie anywhere within the unit area of the surface so that the chance that it lies in  $q_1 - A_2(r)$  is given by the fraction of the total (unit) area which  $q_1 - A_2(r)$  represents. Since there are N-1 choices for this particle, the chance that any one center lies in  $q_1 - A_2(r)$  while the

remaining N-2 are outside is

$$p_1 = (N-1)[q_1 - A_2(r)]P[q_1 - A_2(r), N-2], \quad (5)$$

where  $P[q_1 - A_2(r), N-2]$  is the chance that the remaining N-2 particles are outside the designated area. *P* is close to unity. Indeed, as  $N \rightarrow 0$ ,  $P \rightarrow 1$ . Thus the leading term in an expansion of *P* in powers of *N* is of order zero.

As a result, to first order in N

$$p_1 = N[q_1 - A_2(r)]. (6)$$

It should also be clear that  $p_2$  must be of order  $N^2$ . Thus, we may write

$$p_0 = 1 - [q_1 - A_2(r)]N + O(N^2).$$
(7)

Now the total area accessible to the center of the new particle is  $1-q_1N+O(N^2)$ , so that the chance  $\bar{p}(r,N)r dr d\theta$  that it adsorbs in  $r dr d\theta$  is

$$\bar{p}(r,N)r\,dr\,d\theta = \left\{\frac{1 - [q_1 - A_2(r)]N + O(N^2)}{1 - q_1N + O(N^2)}\right\}r\,dr\,d\theta$$
$$= \{1 + NA_2(r) + O(N^2)\}r\,dr\,d\theta. \tag{8}$$

Then we arrive at the following equation for  $N_2(r,N)$ :

$$\frac{dN_2(r,N)}{dN} = 2\pi r \bar{p}(r,N)N$$
$$= 2\pi r \{1 + NA_2(r) + O(N^2)\}N.$$
(9)

Integrating (9) with respect to the initial condition  $N_2(r, N=0)=0$  and substituting in (1) and (3) we obtain

$$\phi_{\rm RSA} = 1 - Nq_1 + \frac{1}{2}N^2 \int_{\sigma}^{2\sigma} 2\pi r A_2(r) dr + \frac{1}{3}N^3 \int_{\sigma}^{2\sigma} 2\pi r A_2^2(r) dr - S_3^{\rm RSA} + O(N^4) , \qquad (10)$$

where the suffix RSA distinguishes  $S_3^{RSA}$  from  $S_3^{eq}$ , the quantity referring to the equilibrium situation. This is the basic relation for RSA kinetics of disks on a surface. The first two integrals in (10) can be evaluated analytically. However, the direct calculation of  $S_3^{RSA}$  is not obvious. A key observation is that, to order  $N^3$ ,  $S_3^{RSA} = S_3^{eq}$ . For equilibrium configurations  $\rho^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = N^3 + O(N^4)$ .<sup>14</sup> On the other hand, for an RSA process, up to the order of  $N^2$ , we have

$$\frac{dN_3^{\text{KSA}}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3}{dN} = [N_2(\mathbf{r}_1, \mathbf{r}_2) + N_2(\mathbf{r}_1, \mathbf{r}_3) + N_2(\mathbf{r}_2, \mathbf{r}_3)] d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 = [3N^2 + O(N^3)] d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3.$$
(11)

After integrating we find that  $N_3^{\text{RSA}}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = N^3 + O(N^4)$ . Equation (2) then implies that  $S_3^{\text{RSA}} = S_3^{\text{eq}} + O(N^4)$ . We therefore proceed by determining  $\phi_{\text{eq}}$  from (1) and representing it in terms of the virial coefficient. In the equilibrium case:

$$N_2(r) = \frac{1}{2} N^2 2\pi r g(r) , \qquad (12)$$

where g(r) is the pair equilibrium correlation function. Expanding g(r) to first order in N, we have<sup>16</sup>  $g(r) = g_0(r) + Ng_1(r) + O(N^2)$  where  $g_0(r) = H(r - \sigma)$  and

$$g_{1}(r_{12}) = H(r_{12} - \sigma) \int f(\mathbf{r}_{13}) f(\mathbf{r}_{23}) d\mathbf{r}_{3}$$
$$= H(r_{12} - \sigma) A_{2}(r_{12}) .$$
(13)

Here,  $f(r) = e^{-u(r)/kT} - 1$  is the Mayer f function<sup>16</sup> and H(x) is the Heaviside (unit step) function. Thus

$$\phi_{eq} = 1 - Nq_1 + \frac{1}{2} N^2 \int_{\sigma}^{2\sigma} 2\pi r A_2(r) dr + \frac{1}{2} N^3 \int_{\sigma}^{2\sigma} 2\pi r A_2^2(r) dr - S_3^{eq} + O(N^4).$$
(14)

Comparing (10) and (14) we find, with Widom,<sup>4</sup> that terms to order  $N^2$  are identical. From scaled particle theory,<sup>17</sup> or the statistical geometric approach<sup>18</sup> the chemical potential of the hard-sphere system is related to  $\phi_{eq}$  by

$$\mu = \mu_0 + kT \ln N - kT \ln \phi_{eq} , \qquad (15)$$

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where  $\mu_0$  and kT have their usual meaning. The Gibbs-Dehum equation then leads to

$$\phi_{eq} = 1 - 2B_2 N + (B_2^2 - \frac{3}{2}B_3)N^2 + [3B_2 B_3 - \frac{4}{3}(B_2^3 + B_4)]N^3 + O(N^4), \quad (16)$$

where  $B_k$  is the kth virial coefficient. Hence by comparing (14) and (16):

$$S_{3}^{\text{eq}}/N^{3} = \frac{1}{2} \int_{\sigma}^{2\sigma} 2\pi r A_{2}^{2}(r) dr - 3B_{2}B_{3} + \frac{4}{3} (B_{2}^{3} + B_{4}) + O(N). \quad (17)$$

By use of the known values of  $B_2$ ,  $B_3$ , and  $B_4$ , <sup>19</sup> we then have

$$\phi_{\text{RSA}} = dN/dt = 1 - 4\theta + 6\sqrt{3}/\pi\theta^2 + \left(\frac{40}{\sqrt{3}}\frac{1}{\pi} - \frac{176}{3\pi^2}\right)\theta^3 + O(\theta^4), \quad (18)$$

where  $\theta = \pi \sigma^2 N/4$ . In the equilibrium case, the coefficient of  $\theta^3$  is 2.4243.

To test the range of validity of (18) we determined dN/dt as a function of coverage with use of computer simulations. We give full details of these calculations elsewhere, but briefly, hard disks are placed at random, subject to the RSA constraints, in a square cell with periodic boundary conditions. dN/dt is equal to  $1/\langle N_A(N) \rangle$  where  $N_A(N)$  is the number of attempts to adsorb the Nth particle and angular brackets denote an average over separate simulations. Our results represent an average of 25000 such simulations. It can be seen from Fig. 1 that the  $\theta^3$  term represents more than a



FIG. 1. Rate of adsorption, dN/dt, as a function of surface coverage,  $\theta = \pi \sigma^2 N/4$ . The solid curve shows the averaged results of computer simulations where each disk has an area relative to the surface of 0.002. The dotted line shows the expansion (16) to order  $\theta^2$ ; the dashed line shows the expansion (16) to order  $\theta^3$ .

small correction in the intermediate coverage range. With this term, RSA kinetics are described accurately up to a coverage of about 0.3. At higher coverages, we enter the asymptotic regime (eventually the jamming limit) where the kinetics are well known.<sup>6,7</sup> Thus we now have an almost complete description of the RSA process.

Since adsorption experiments are very difficult to perform close to the jamming limit, the most effective way to demonstrate that adsorption follows an RSA process is to measure the  $\theta_3$  term of (18). In this context, it is important to emphasize that terms up to and including  $\theta^2$  contain no information concerning the nature of the adsorption process (i.e., the degree of irreversibility). This implies that such an expansion (to second order) applies to any adsorption experiment of hard disklike particles.

Our method can be extended to noncircular particles and mixtures. In the latter case it is necessary to introduce two  $\phi$  functions and correspondingly two coupled nonlinear equations.

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177

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