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Random sequential adsorption of hard discs and squares: exact bounds for the covering fraction

S Caser and H J Hilhorst

Laboratoire de Physique Théorique et Hautes Energies†, Bâtiment 211, Université de Paris-Sud, 91405 Orsay Cédex, France

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Abstract. We investigate the random sequential adsorption of hard discs and hard aligned squares onto a plane, by a new series expansion method that we previously devised for a lattice. The method yields sequences of increasing lower bounds for the time-dependent covering fraction $\Theta(t)$. These bounds have non-trivial limit values for $t \to \infty$, i.e. for the saturated state. Hypercubes and an analytic continuation in the dimension D around $D = 0$ are also considered. Numerical results are given for the lowest orders in the series.

1. Introduction

Random sequential adsorption (RSA) is the physical process in which vapour particles of one substance are deposited sequentially onto a substrate of a different material. Once deposited a particle does not move and excludes its neighbourhood from being occupied by the next particle. There is supposed to be a constant incident flux of particles onto the substrate, with attempts to deposit them taking place at random locations. No second layer particles are allowed and only attempts that do not violate the excluded surface condition are successful. As time increases, the substrate will therefore tend to a saturated state in which no more particles can be adsorbed. The primary quantity of physical interest is the covering fraction $\Theta(t)$ as a function of time t, that is, the fraction of the substrate area covered by adsorbed particles. A recent review by Evans [1] describes the various theoretical models that have been studied to investigate the RSA process. Recent experimental techniques have been discussed by Ramsden [2].

Much of our knowledge about RSA comes from numerical simulations. Exact results (in two dimensions) are virtually non-existent. The best analytical estimates of $\Theta(t)$ are based on the extrapolation of initial time expansions [3]. In this paper we describe an expansion method that provides rigorous lower bounds on $\Theta(t)$. The bounds have a non-trivial $t \to \infty$ limit and can be successively improved by the calculation of higher-order terms. Our expansion method is based on an idea first conceived as a new numerical algorithm for lattice RSA. Subsequently it was converted into an analytical expansion scheme and yielded exact bounds [4] for lattice RSA. In this paper we describe its implementation in continuous space, which differs considerably from its lattice version. The result is a systematic series of only positive terms that converges to $\Theta(t)$. We present the lowest-order terms for hard discs and hard squares. The numerical values of these lowest-order bounds still fall considerably

† Laboratoire associé au Centre National de la Recherche Scientifique.

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below the best estimates by other methods. They are of interest because they constitute exact results in a field where there are very few, and because of the potential of the method.

In section 2 we describe our formalism for the RSA of hard discs of radius a. In section 3 we describe how an increasing series can be obtained for $\Theta(t)$, with, as a special case, $\Theta(\infty)$. The terms in the series can be classified as coming from diagrams with one, two, three,... 'participating' discs. In the end, an m-disc contibution can be expressed as an integral on the positions of m overlapping discs of *radius* $2a$, with an integrand that is a function of the different areas of overlap. Although superficially reminiscent of a virial expansion [3], our method is distinctively different from the virial approach and cannot be simply related to it. In sections 4 and 5 we explore some further possibilities of the method. In section 4 we consider hard aligned squares in an arbitrary dimension D, and find the lowest-order bound for $\Theta(\infty)$. The result suggests that, upon analytic continuation in D, the $D = 0$ result for the saturated state is *exactly* $\Theta(\infty) = 1$. In section 5 we therefore consider the dimension $D = 0 + \epsilon$ and set up a double expansion, in ϵ and in the number m of participating discs. The 2-disc term in the series for $\Theta(\infty)$ calculated to order ϵ and extrapolated to $D = 1$ and $D = 2$ can no longer be considered as a bound, but comes close to the simulation values. Section 6 contains our conclusions.

2. RSA of hard discs

2.1. *Definition of the process*

We consider the RSA of hard discs of radius a onto a perfectly flat substrate of area V, subject to an incident flux of j discs per unit of surface and of time. Attempts to deposit a disc will be supposed to take place at regular time intervals $\Delta t, 2\Delta t, 3\Delta t, \ldots, N\Delta t, \ldots$ where $\Delta t = (Vj)^{-1}$. Units will be chosen such that $j = 1$. We shall eventually be interested in the limit

$$N \to \infty \qquad V \to \infty \qquad N\Delta t = N/V \equiv t \quad \text{fixed} \tag{2.1}$$

where t is the physical time, and shall want to study the configuration of adsorbed discs at time t. The time evolution up to time t is uniquely determined by the ordered list of spatial locations $\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_N$ where the first N attempts (successful or not) of depositing a disc took place. Below we describe two algorithms for constructing the adsorbed configuration at time t given this list of 'attempt locations'.

2.2. *The usual algorithm*

In the usual algorithm for simulation of RSA, one first places a disc at $\vec{R}_1$. Then, letting ν successively take the values $2, 3, \ldots, N$, one places a disc at $\vec{R}_\nu$ if and only if none of the attempt locations $\vec{R}_i \in \{\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_{\nu-1}\}$ *where a disc has previously been placed* falls within an exclusion disc of radius $2a$ around $\vec{R}_\nu$. In this algorithm, the configuration of all discs placed after one has considered $\vec{R}_\nu$ represents the physical configuration of adsorbed discs at time $\nu\Delta t \equiv \tau$. In this way the list $\vec{R}_1, \ldots, \vec{R}_N$ yields the time evolution of the physical configuration for all times $0 \leqslant \tau \leqslant t$. We recall here this well known fact in order to contrast it with a different algorithm to be discussed now.

2.3. *The sweep algorithm*

This is a different algorithm for deriving the configuration of adsorbed discs at time $t \equiv N\Delta t$ from the list $\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_N$. We do not advocate this algorithm as a serious alternative to the usual one for practical simulations. It is presented here because it provides the key idea for a new analytic approach. It is close in spirit to the sweep algorithm that we described [4] for lattice RSA, but working in continuous space makes its implementation very different.

The sweep algorithm goes as follows. The list of attempt locations $\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_N$ is gone through alternately with two kinds (A and B) of sweeps that we denote $1A$, $1B$, $2A$, $2B, \ldots$. In type A sweeps, discs may be placed at attempt locations of the list, in type B sweeps the list is shortened by deletion of locations. Here is the precise definition.

Sweep 1A. Place a disc at $\vec{R}_1$. For $\nu = 2, 3, \ldots, N$ place a disc at the location $\vec{R}_\nu$ if and only if none of the attempt locations $\vec{R}_1, \ldots, \vec{R}_{\nu-1}$, *whether or not a disc has been placed on it*, falls within an exclusion disc of radius $2a$ around $\vec{R}_\nu$. Therefore if a disc has been placed at $\vec{R}_\nu$ during sweep $1A$, an attempt location $\vec{R}_\mu$ can fall within its exclusion disc only if $\nu + 1 \leqslant \mu \leqslant N$.

Sweep 1B. All locations where discs have been placed during sweep $1A$, as well as all attempt locations that fall within their exclusion discs, are deleted from the list (but the adsorbed discs remain in place). The order of the locations that stay in the list remains unchanged. This results in a shortened list $\vec{R}_1^{(1)}, \vec{R}_2^{(1)}, \ldots, \vec{R}_{N_1}^{(1)}$ with $N_1 \leqslant N - 1$.

For $n = 2, 3, \ldots$ the sweep nA has as its input the ordered list $\vec{R}_1^{(n-1)}, \vec{R}_2^{(n-1)}, \ldots, \vec{R}_{N_{n-1}}^{(n-1)}$. It is defined as follows.

Sweep nA. Place a disc at $\vec{R}_1^{(n-1)}$. For $\nu = 2, 3, \ldots, N_{n-1}$ place a disc at $\vec{R}_\nu^{(n-1)}$ if and only if none of the attempt locations $\vec{R}_1^{(n-1)}, \ldots, \vec{R}_{\nu-1}^{(n-1)}$ fall within an exclusion disc of radius $2a$ around $\vec{R}_\nu^{(n-1)}$.

Sweep nB. All locations where discs have been placed during sweep nA, as well as all attempt locations that fall within their exclusion discs, are deleted from the list. The order of the locations that stay in the list remains unchanged. This results in a shortened list $\vec{R}_1^{(n)}, \vec{R}_2^{(n)}, \ldots, \vec{R}_{N_n}^{(n)}$ with $N_n \leqslant N_{n-1} - 1$.

The algorithm stops when shortening leads to an empty list. On the basis of our experience with simulations we expect that typically the number of sweeps needed increases at most logarithmically with N and hence, at fixed time t, with the system size V.

Every disc that is placed in a sweep of type A is necessarily also placed in the real adsorption process, because the condition on placing a disc in a type A sweep is more stringent than in the real process. Conversely, every disc placed in the physical process will end up by being placed, for some n, in a type A sweep. Therefore at the end of the algorithm the configuration of placed discs represents the physical configuration of adsorbed discs at time $t \equiv N/V$. One cannot attach a direct physical meaning to the intermediate configurations that prevail after the sweeps $1A, 2A, 3A, \ldots$. But since the covering fraction $\Theta_n(t)$ after sweep nA is an increasing function of n, one has that $\Theta_1(t), \Theta_2(t), \Theta_3(t), \ldots$ forms an increasing sequence of lower bounds converging to the physical covering fraction $\Theta(t)$ at time t. At the basis of the exact bounds presented in this work are this observation and the fact that each $\Theta_n(t)$ can be calculated, in principle, at the cost of a finite amount of effort.

3. Increasing series for the covering fraction $\Theta(t)$ of hard discs

3.1. The basic series

Each time an attempt to place a disc is successful, the covering fraction increases by $\pi a^2/V$. The total covering fraction $\Theta(t)$ at time t is therefore equal to

$$\Theta(t) = \frac{\pi a^2}{V} \sum_{\nu=1}^{N} \overline{\Delta_\nu(\vec{R}_1, \vec{R}_2, \ldots \vec{R}_\nu)} \tag{3.1}$$

where $\Delta_\nu = 1$ ($\Delta_\nu = 0$) if the attempt to adsorb a disc at $\vec{R}_\nu$ is successful (unsuccessful); we have indicated that this quantity only depends on the first ν elements of the full list $\vec{R}_1, \ldots, \vec{R}_N$, and the overbar represents the average over all attempt lists, obtainable by letting $\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_N$ vary independently through the surface V.

We now make use of the sweep algorithm to write

$$\Delta_\nu = \sum_{n\geqslant 1} \Delta_\nu^{(n)} \tag{3.2}$$

where $\Delta_\nu^{(n)}(\vec{R}_1, \ldots, \vec{R}_\nu) = 1$ (or $= 0$) if an adsorption in $\vec{R}_\nu$ takes place (or does not take place) during sweep nA. Upon combining (3.1) and (3.2) and rendering the average explicit we get

$$\Theta(t) = \sum_{n=1}^{\infty} \Theta_n(t) \tag{3.3}$$

where

$$\Theta_n(t) = \frac{\pi a^2}{V} \sum_{\nu=1}^{N} p_{n,\nu} \tag{3.4}$$

with

$$p_{n,\nu} = \int_V \cdots \int_V \prod_{\mu=1}^{\nu} \frac{\mathrm{d}\vec{R}_\mu}{V} \Delta_\nu^{(n)}(\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_\nu) \tag{3.5}$$

the probability that the sweep nA of the sweep algorithm leads to placing a disc at the νth attempt location. The dependence on time t in the LHS of (3.4) is a consequence only of the summation in the RHS ending at the upper limit $N = Vt$. In all of the above expressions the large-system limit $N \to \infty$, $V \to \infty$ with $N/V = t$ fixed should be taken. It will appear that in this limit the probability $p_{n,\nu}$ only depends on the ratio $\tau = \nu/V$, of which it is a slowly varying function. Anticipating upon this result and setting

$$p_{n,\nu} = p_n(\tau) \qquad (\nu, V \to \infty \text{ with } \nu/V = \tau \text{ fixed}) \tag{3.6}$$

we can therefore write (3.4) as

$$\Theta_n(t) = \pi a^2 \int_0^t \mathrm{d}\tau \, p_n(\tau). \tag{3.7}$$

Equation (3.3) is the basic series, and we shall now see how the successive terms can be evaluated.

3.2. The first term

The $n = 1$ term in (3.3) is a sum on ν of the probability $p_{1,\nu}$ that during the sweep $1A$ a disc is placed at the νth attempt location. This will happen if $\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_{\nu-1}$ are all outside of the exclusion disc of radius $2a$ around $\vec{R}_\nu$. The expression for this probability, given by (3.5), is therefore easy to evaluate and we find

$$p_{1,\nu} = (1 - 4\pi a^2/V)^{\nu-1} \tag{3.8a}$$

or equivalently, in the large-system limit,

$$p_1(\tau) = \mathrm{e}^{-4\pi a^2 \tau}\,. \tag{3.8b}$$

Combined with (3.7) and (3.3) this gives straightforwardly the time-dependent lower bound

$$\begin{aligned} \Theta(t) > \Theta_1(t) &= \pi a^2 \int_0^t \mathrm{d}\tau\, \mathrm{e}^{-4\pi a^2 \tau} \\ &= \tfrac{1}{4}\left(1 - \mathrm{e}^{-4\pi a^2 t}\right). \end{aligned} \tag{3.9}$$

For $t \to \infty$ this gives as a special case the lower bound

$$\Theta(\infty) > \tfrac{1}{4} \tag{3.10}$$

for the covering fraction in the saturated state. This lower bound is simple to interpret geometrically: it is the ratio of the area of a disc to the area of its exclusion disc. In spite of the elementary nature of this calculation, equation (3.9) is to our knowledge the first exact positive lower bound for $\Theta(t)$ ever presented.

3.3. Higher terms. Expansion in the number of participating discs

Let us consider $\Theta_2(t)$ in (3.3). Its calculation requires the determination of the probability $p_{2,\nu}$ that at the νth attempt location $\vec{R}_\nu$ a disc is placed during the sweep $2A$. For this to happen, a set $\{\vec{R}_{\nu'}\}$ of one or more attempt locations with index $\nu' < \nu$ in the exclusion disc around $\vec{R}_\nu$ must have prevented this disc from being placed during sweep $1A$, and each $\vec{R}_{\nu'}$ must have been eliminated from the list by also being in the exclusion disc of at least one disc placed during sweep $1A$. Let $\{\vec{R}_{\mu_1}, \vec{R}_{\mu_2}, \ldots, \vec{R}_{\mu_s}\}$ be the full set of discs placed during sweep $1A$ and having one or more of the $\vec{R}_{\nu'}$ in their exclusion discs. An example of a diagram representing the situation with $s = 3$ is depicted in figure 1. We shall say that this is a diagram of four *participating* (= actually placed) *discs*.

Before proceeding further we still make the following observations about this diagram. First, the s discs of type $1A$ may not have all been needed to eliminate the set of points $\{\vec{R}_{\nu'}\}$. For example, in figure 1, the disc at $\vec{R}_{\mu_2}$ is superfluous. Nevertheless, for each attempt location $\vec{R}_\nu$ filled during sweep $2A$, the set of participating discs is uniquely defined. Second, an attempt location $\vec{R}_{\nu'}$ in the intersection of the exclusion discs around $\vec{R}_{\mu_1}$ and $\vec{R}_\nu$ must have its index ν' between μ_1 and ν.

The probability $p_{2,\nu}$ can be decomposed as a sum of contributions $p_{2,\nu}^{(m)}$ coming from diagrams with m participating discs. More generally we shall write

$$p_{n,\nu} = \sum_{m=n}^{\infty} p_{n,\nu}^{(m)}\,. \tag{3.11}$$

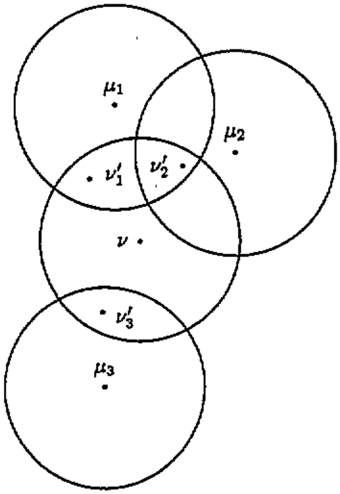

Figure 1. A diagram with four participating discs contributing to Θ_2. Whereas the discs have radius a, the circles shown correspond to their excluded area and have radius $2a$.

Geometric constraints on the way to place the discs will render the number of terms in the sum on m finite. In particular, $p_{1,\nu} = p_{1,\nu}^{(1)}$ (there is only one participating disc in the lowest-order approximation).

By substituting (3.11) in (3.4) and (3.3) one gets

$$\Theta(t) = \frac{\pi a^2}{V} \sum_{\nu=1}^{N} \sum_{n=1}^{\infty} \sum_{m=n}^{\infty} p_{n,\nu}^{(m)} \tag{3.12}$$

or, equivalently

$$\Theta(t) = \sum_{m=1}^{\infty} \sum_{n=1}^{m} \Theta_n^{(m)}(t) \tag{3.13}$$

where

$$\Theta_n^{(m)}(t) = \frac{\pi a^2}{V} \sum_{\nu=1}^{N} p_{n,\nu}^{(m)} \qquad (m \geqslant n \geqslant 1) \tag{3.14}$$

is the contribution of m participating discs to $\Theta_n(t)$. In particular, $\Theta_1 = \Theta_1^{(1)}$. In the large-system limit equation (3.14) becomes

$$\Theta_n^{(m)}(t) = \pi a^2 \int_0^t \mathrm{d}\tau\, p_n^{(m)}(\tau) \qquad (m \geqslant n \geqslant 1) \tag{3.15}$$

which is the contribution to (3.7) from m participating discs.

Equation (3.13) is a double expansion of $\Theta(t)$, in the number m of participating discs and in the index n of the sweep algorithm. All terms in this expansion are positive. Hence the sum of any finite number of them gives a lower bound that increases when terms are added. Obviously there are many ways to rearrange the terms. In the calculations that follow we have found it convenient to classify the contributions to the lower bound according to the number of participating discs.

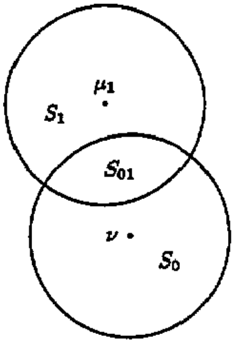

Figure 2. The simplest diagram contributing to Θ_2, with two participating discs.

3.4. Two-disc contribution

There is a two-disc contribution only to $\Theta_2(t)$. The two-disc contribution $\Theta_2^{(2)}(t)$ requires the calculation of $p_{2,\nu}^{(2)}$, which can be represented by the diagram of figure 2, in which the relevant areas are labelled S_0, S_{01} and S_1. This diagram represents the integral of (3.5) for the case $n = 2$, restricted to two participating discs, of which one is placed in $\vec{R}_\nu$, and one in another arbitrary location $\vec{R}_{\mu_1}$ with the index μ_1 to be summed over. The points $\vec{R}_1$, $\vec{R}_2, \ldots, \vec{R}_\nu$ contributing to the integral fall into two different sets:

Set O. The points with an index between 1 and $\mu_1 - 1$ are excluded from the whole area $S_0 + S_{01} + S_1$. The integration on these points gives a factor $[1 - (S_0 + S_{01} + S_1)/V]^{\mu_1 - 1}$.

Set I. The remaining points, $\vec{R}_{\mu_1+1}$ to $\vec{R}_{\nu-1}$, must all lie outside S_0, with at least one of them in the intersection S_{01} (for the $1B$ step of the sweep algorithm to be effective). Therefore the set I cannot be empty. The corresponding factor in $p_{2,\nu}$, as given by the integration in (3.5), can be obtained by excluding all points from S_0, and subtracting from this the contribution with all points excluded from both S_0 *and* S_{01}. This yields the factor $(1 - S_0/V)^{\nu-1-\mu_1} - [1 - (S_0 + S_{01})/V]^{\nu-1-\mu_1}$.

We therefore get

$$p_{2,\nu}^{(2)} = \sum_{\mu_1=1}^{\nu-2} \int_V \frac{d\vec{R}_\nu}{V} \int \frac{d\vec{R}_{\mu_1}}{V} \left(1 - \frac{S_0 + S_{01} + S_1}{V}\right)^{\mu_1 - 1} \times \left[\left(1 - \frac{S_0}{V}\right)^{\nu-1-\mu_1} - \left(1 - \frac{S_0 + S_{01}}{V}\right)^{\nu-1-\mu_1}\right]. \tag{3.16}$$

In the large-system limit, we set $\tau = \nu/V$ and $\sigma = \mu_1/V$. The sum on μ_1 becomes an integral on σ and can be interchanged with the integration on $\vec{R}_{\mu_1}$. Since the integrand only depends on $\vec{R} \equiv \vec{R}_{\mu_1} - \vec{R}_\nu$ (and, in fact, only on R) we get

$$p_2^{(2)}(\tau) = \int d\vec{R} \int_0^\tau d\sigma\, e^{-(S_0+S_{01}+S_1)\sigma} e^{-S_0(\tau-\sigma)} \left[1 - e^{-S_{01}(\tau-\sigma)}\right]. \tag{3.17}$$

Since $S_0 = S_1 = 4\pi a^2 - S_{01}$, the integrand can be expressed as a function of S_{01} only; however, in (3.17), we wanted to display the overall factor explicitly outside the brackets. This factor takes into account the excluded areas for the sets O and I, as explained above.

A factor of this type, suitably generalized, will appear in each contributing term in the large-system limit.

Combining (3.17) with (3.15), we find

$$\Theta_2^{(2)}(t) = \frac{1}{4}\int \frac{\mathrm{d}\vec{R}}{4\pi a^2 - S_{01}}\left[\frac{S_{01}}{8\pi a^2 - S_{01}}\left(1 - \mathrm{e}^{-(8\pi a^2 - S_{01})t}\right) + \mathrm{e}^{-4\pi a^2 t} - \mathrm{e}^{-(4\pi a^2 - S_{01})t}\right] \tag{3.18}$$

in which S_{01} is a function of R. For $t \to \infty$ this gives the contribution

$$\Theta_2^{(2)}(\infty) = \frac{1}{4}\int \mathrm{d}\vec{R}\frac{S_{01}}{(4\pi a^2 - S_{01})(8\pi a^2 - S_{01})} \tag{3.19a}$$

$$= \frac{1}{4}\int_{2a}^{4a} 2\pi R\,\mathrm{d}R\frac{S_{01}}{(4\pi a^2 - S_{01})(8\pi a^2 - S_{01})} \tag{3.19b}$$

to the covering fraction $\Theta(\infty)$ in the saturated state, to be added to the lower bound $\frac{1}{4}$ of (3.10).

For the purpose of analogy with what follows we remark that if one is only interested in the limit $t \to \infty$, one may consider (3.15) directly with $n = m = 2$ and $t = \infty$, and change variables to $u_0 = \sigma$, $u_1 = \tau - \sigma$, where u_0 and u_1 correspond to the sets O and I, respectively, and both run from 0 to ∞. Thus,

$$\Theta_2^{(2)}(\infty) = \pi a^2 \int \mathrm{d}\vec{R}\int_0^\infty \mathrm{d}u_0 \int_0^\infty \mathrm{d}u_1\,\mathrm{e}^{-(S_0+S_{01}+S_1)u_0}\mathrm{e}^{-S_0 u_1}\left[1 - \mathrm{e}^{-S_{01}u_1}\right] \tag{3.20}$$

which can readily be integrated to yield (3.19).

By expressing R and S_{01} as functions of the angle ϕ under which the chord common to the two-disc perimeters is seen from the centre of either disc, one can write (3.19*b*) in the form

$$\Theta_2^{(2)}(\infty) = \frac{\pi}{2}\int_0^{2\pi/3} \mathrm{d}\phi\,\frac{(\phi - \sin\phi)\sin\phi}{(\pi - \phi + \sin\phi)(2\pi - \phi + \sin\phi)}\,. \tag{3.21}$$

The disc radius a has dropped out of this result, as it should. Numerical evaluation of (3.21) gives an extra contribution of 0.078 to $\Theta(\infty)$. The lower bound for $\Theta(\infty)$ coming from up to two participating discs, as given by (3.21) and (3.10), is therefore equal to 0.328, still far away from the value of 0.547 obtained by simulation [1].

To further illustrate the method, in the following section we consider the case of three discs. Since no new numbers are given, the reader with a purely numerical interest may turn directly to section 4.

3.5. Three-disc contribution

The expansion (3.13) contains two three-disc terms, $\Theta_2^{(3)}$ and $\Theta_3^{(3)}$, that contribute to Θ_2 and Θ_3, respectively. We shall consider them successively. The contribution $\Theta_2^{(3)}$ requires the calculation of $p_{2,\nu}^{(3)}$, which involves three participating discs of which one is placed in

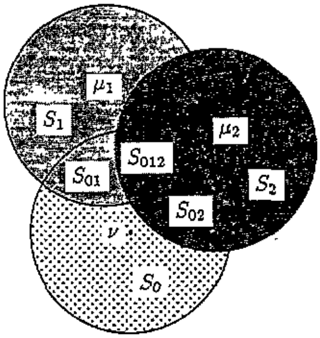

Figure 3. A diagram with three participating discs contributing to Θ_2.

$\vec{R}_\nu$ and the two other ones in arbitrary locations $\vec{R}_{\mu_1}$ and $\vec{R}_{\mu_2}$ with the indices μ_1 and μ_2 to be summed over. This is shown in figure 3. The areas S_{12} and S_{012} will be zero for certain configurations of the discs. We shall write the expression for $\Theta_2^{(3)}$ in the large-system limit directly. We set $\nu = \tau/V$, $\sigma_1 = \mu_1/V$ and $\sigma_2 = \mu_2/V$, with $0 < \sigma_1 < \sigma_2 < \tau$, and let N and V go to ∞ with $N/V = t$ as before. This defines three sets of indices, which we label O, I, and II. We introduce corresponding time difference variables

$$u_0 = \sigma_1 \qquad u_1 = \sigma_2 - \sigma_1 \qquad u_2 = \tau - \sigma_2 . \tag{3.22}$$

Although the full advantage of the variables u only appears in the $t \to \infty$ limit when they vary independently from 0 to ∞, they also make the finite t expressions somewhat easier to handle.

The first set of points, O, is excluded from the union of the three discs of figure 3, the second set, I, from the dark gray and dotted areas, and the third set, II, from the dotted area only. This gives an overall exclusion factor of

$$q_1(u_0, u_1, u_2) \equiv e^{-Su_0} e^{-(S-S_1-S_{01})u_1} e^{-S_0 u_2} \tag{3.23}$$

where $S = S_0 + S_1 + S_2 + S_{01} + S_{02} + S_{12} + S_{012}$. We should now multiply this by an extra factor q_2 which takes into account the supplementary conditions to be obeyed by the points in sets I and II. As we can see from the previous example, the appearance of these conditions as a factor is characteristic of the large-system limit. These conditions can be expressed in terms of the following three propositions.

(i) There is at least one point of II in S_{012}.
(ii) There is at least one point of I, or one point of II, in S_{01}.
(iii) There is at least one point of II in S_{02}.

A careful examination of the different possibilities leading to $\Theta_2^{(3)}$ shows that the correction factor q_2 we are looking for is given by the probability p that either α is true, or β *and* γ are true, that is by

$$\begin{aligned} q_2 = p(\alpha \cup (\beta \cap \gamma)) &= p(\alpha) + p(\beta \cap \gamma) - p(\alpha \cap \beta \cap \gamma) \\ &= p(\alpha) + p(\beta)p(\gamma) - p(\alpha)p(\beta)p(\gamma) . \end{aligned} \tag{3.24}$$

Indeed, in the large-system limit, one can easily convince oneself that the three propositions imply independent constraints on the points of the sets. This is the reason for the factorization in the second equality (3.24). It is straightforward to write the corresponding probabilities:

$$p(\alpha) = 1 - \mathrm{e}^{-S_{012}u_2} \qquad p(\beta) = 1 - \mathrm{e}^{-S_{01}(u_1+u_2)} \qquad (\gamma) = 1 - \mathrm{e}^{-S_{02}u_2}\,. \tag{3.25}$$

Hence,

$$q_2(u_1, u_2) = 1 + \mathrm{e}^{-S_{012}u_2}\left(\mathrm{e}^{-S_{01}(u_1+u_2)-S_{02}u_2} - \mathrm{e}^{-S_{01}(u_1+u_2)} - \mathrm{e}^{-S_{02}u_2}\right). \tag{3.26}$$

All the areas $S_0, \ldots, S_{012}$ appearing in (3.23) and (3.26) can easily be expressed explicitly as functions of the two relative positions $\vec{R}_1 \equiv \vec{R}_{\mu_1} - \vec{R}_\nu$ and $\vec{R}_2 \equiv \vec{R}_{\mu_2} - \vec{R}_\nu$. We now multiply (3.26) by (3.23) and integrate on $\vec{R}_1$ and $\vec{R}_2$. The sums on μ_1 and μ_2 become integrals on σ_1 and σ_2, respectively, and yield $p_{2,\nu}^{(3)}$. The quantity $\Theta_2^{(3)}$ is obtained, as shown in (3.14), by a sum on ν which becomes an integral on t, so that finally

$$\Theta_2^{(3)}(t) = \pi a^2 \int \mathrm{d}\vec{R}_1 \int \mathrm{d}\vec{R}_2 \int_0^t \mathrm{d}\tau \int_0^\tau \mathrm{d}\sigma_2 \int_0^{\sigma_2} \mathrm{d}\sigma_1\, q_1(u_0, u_1, u_2) q_2(u_1, u_2) \tag{3.27}$$

where u_0, u_1 and u_2 are given in terms of σ_1, σ_2, τ by (3.22). The corresponding contribution to the covering fraction in the saturated state is

$$\Theta_2^{(3)}(\infty) = \pi a^2 \int \mathrm{d}\vec{R}_1 \int \mathrm{d}\vec{R}_2 \int_0^\infty \mathrm{d}u_0 \int_0^\infty \mathrm{d}u_1 \int_0^{\epsilon f/y} \mathrm{d}u_2\, q_1(u_0, u_1, u_2) q_2(u_1, u_2) \tag{3.28}$$

where the outer space integral is simply $\int_{2a}^{4a} 2\pi R_1\, \mathrm{d}R_1$, while the limits of the inner integral depend on R_1.

We conclude this section by considering the other three-disc term, namely $\Theta_3^{(3)}$, in the large-system limit. The relevant diagram is shown in figure 4. As in the previous diagram,

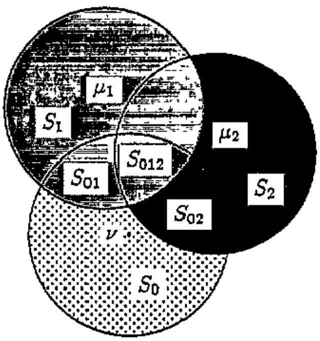

Figure 4. The simplest contribution to Θ_3, with three participating discs.

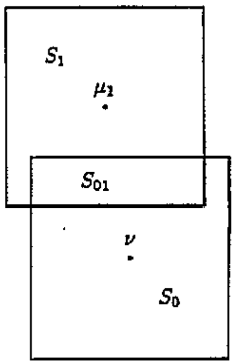

Figure 5. The simplest contribution to Θ_2, with two participating squares.

some of the areas, namely S_{01} and S_{012}, may not exist for all configurations of the discs. All areas and sets of variables are defined as before. The set O is excluded from the union of the three discs, the set I from the dark gray and dotted areas, the set II from the dotted area. This gives the overall exclusion factor

$$q_1(u_0, u_1, u_2) = \mathrm{e}^{-Su_0}\mathrm{e}^{-(S_0+S_2+S_{02})u_1}\mathrm{e}^{-S_0u_2}\,. \tag{3.29}$$

The extra factor q_2 comes from the consideration of the following two propositions:

(i) There is at least one point of I in $S_{12} + S_{012}$.
(ii) There is at least one point of II in S_{02}.

These propositions must be true simultaneously. Hence

$$q_2(u_1, u_2) = p(\alpha \cap \beta) = p(\alpha)p(\beta) \tag{3.30}$$

where the factorization in the second equality is exact even for a finite system due to the independence of the variables in sets I and II. The corresponding probabilities can readily be written down as

$$p(\alpha) = 1 - \mathrm{e}^{-(S_{12}+S_{012})u_1} \qquad p(\beta) = 1 - \mathrm{e}^{-S_{02}u_2}\,. \tag{3.31}$$

Multiplying and integrating as before again yields for $\Theta_3^{(3)}$ the formulae (3.27) and (3.28), but with q_1 and q_2 now given by (3.29)–(3.31).

The integrations on the variables u can be performed, to yield

$$\begin{aligned}\Theta_2^{(3)}(\infty) &= \pi a^2 \int \mathrm{d}\vec{R}_1 \int \mathrm{d}\vec{R}_2\, \frac{1}{S}\left[\frac{S_{02} + S_{012}}{S_0(S - S_1 - S_{01})(S_0 + S_{02} + S_{012})}\right. \\ &\qquad \left. - \frac{S_{02}}{(S - S_1)(S_0 + S_{01} + S_{02} + S_{012})(S_0 + S_{01} + S_{012})}\right] \\ \Theta_3^{(3)}(\infty) &= \pi a^2 \int \mathrm{d}\vec{R}_1 \int \mathrm{d}\vec{R}_2\, \frac{S_{02}(S_{12} + S_{012})}{SS_0(S - S_1 - S_{01})(S_0 + S_{02})(S_0 + S_2 + S_{02})}\,.\end{aligned} \tag{3.32}$$

With these explicit expressions for $\Theta_2^{(3)}$ and $\Theta_3^{(3)}$ we have completed our discussion of the three-disc contributions.

Here we shall not pursue the case of more than three participating discs. It is obvious that the complexity of the calculation increases quickly with the number of participating discs. Considering only the second step of the sweep algorithm ($n = 2$), there may be as many as $m = 13$ participating discs. As already obvious from figures 3 and 4 and the calculation of $\Theta_2^{(3)}$ and $\Theta_3^{(3)}$, the number of overlapping areas and their dependence on the positions of the discs constitute the main difficulty in evaluating the integrals. (Remember, however, that each contribution to (3.13) raises the value of the lower bound, and that the latter is exact.)

4. RSA of hard aligned hypercubes

The discussion of sections 2 and 3 concerns the RSA of hard discs in the plane. Obviously analogous considerations hold for discs in general dimension D ('hyperdiscs'), and for hypercubes. In this section we shall be interested in the RSA of hard aligned hypercubes of side a in dimension D. Clearly in the algorithm of sections 2 and 3 the exclusion disc of radius $2a$ should be replaced by an exclusion hypercube of side $2a$, and the disc surface πa^2, wherever it occurs, by the hypercube volume a^D. Thus, the one-hypercube lower bound $\Theta_1(t)$ for $\Theta(t)$ is still given by

$$\Theta_1(t) = 2^{-D}\left(1 - \mathrm{e}^{-(2a)^D t}\right). \tag{4.1}$$

We next note that the equations (3.18), (3.19a), (3.27), (3.28) and (3.32) that represent the two- and three-disc contributions to the lower bounds for $\Theta(t)$ and $\Theta(\infty)$ hold similarly for hypercubes, at the condition of taking for $S_0, S_1, S_{01}, \ldots$ not the areas of exclusion discs and their intersections, but volumes of exclusion hypercubes and their intersections. The hypercube equivalent of (3.19a) is

$$\Theta_2^{(2)}(\infty) = \frac{1}{2^D}\int \mathrm{d}^D\vec{R}_1 \frac{S_{01}}{[(2a)^D - S_{01}][2(2a)^D - S_{01}]} \tag{4.2}$$

where S_{01} is the volume of the intersection of two hypercubes of side $2a$ whose centres are in the origin and in $\vec{R}$, and the integration is on the volume between the hypercubes of sides $2a$ and $4a$ centred in the origin. We discuss three special dimensions.

(i) In dimension $D = 2$ equation (4.2) reduces to

$$\Theta_2^{(2)}(\infty) = 2\int_0^1 \frac{\mathrm{d}x}{x}\log\left[\left(\frac{x}{2}+1\right)\left(\frac{8-2x}{8-x^2}\right)^2\right]. \tag{4.3}$$

Numerical evaluation of (4.3) yields 0.0845 and hence a value of 0.3345 for the two-square lower bound on $\Theta(\infty)$. The simulation value is 0.562 [1].

(ii) In one dimension, hypercubes (as well as hyperdiscs) reduce to hard rods. The two-rod lower bound to $\Theta(\infty)$ is also easily computed from (4.2):

$$\Theta_1(\infty) + \Theta_2^{(2)}(\infty) = \frac{1}{2} + \int_a^{2a} \mathrm{d}x \frac{S_{01}}{(2a - S_{01})(4a - S_{01})} \tag{4.4}$$

with $S_{01} = 2a - x$. This gives (independently of a)

$$\Theta_1(\infty) + \Theta_2^{(2)}(\infty) = \tfrac{1}{2} + 2\log 3 - 3\log 2 \tag{4.5}$$

which is approximately 0.6178, to be compared with the exact result 0.7476 [1].

5. Expansion of the participating disc and hypercube series around dimension $D = 0$

5.1. The method

The one-hypercube lower bound in D dimensions, equation (4.1), shows that $\Theta_1(\infty)$ goes to 1 as D goes to zero. This fact suggests that we try an expansion of Θ in powers of $D = \epsilon$. If the order in ϵ increased with the number of participating discs (cubes), this would provide us with a justification for retaining only the first few terms in the series (3.13) (in low dimensions at least). Below we shall present the contribution to the order ϵ coming from two participating discs. We think this calculation is interesting even if we cannot be sure that three and more participating discs will not also contribute to order ϵ.

Consider first the case of discs. Equation (3.19a) can be generalized to D dimensions as

$$\Theta_2^{(2)}(\infty) = \frac{1}{2^D} D K_D \int_1^2 \mathrm{d}r\, r^{D-1} \frac{S_{01}}{(K_D - S_{01})(2K_D - S_{01})} . \tag{5.1}$$

The integration measure $\mathrm{d}^D R$ has been written out explicitly by using the distance r between the disc centres (divided by $2a$), and K_D is the volume of the unit sphere in D dimensions:

$$K_D = \frac{\pi^{\frac{D}{2}}}{\Gamma(\frac{D}{2}+1)} . \tag{5.2}$$

S_{01}, as before, is the intersection volume (in D dimensions),

$$S_{01}(r) = 2 \int_{r/2}^{1} \mathrm{d}z \left(\sqrt{1-z^2}\right)^{D-1} K_{D-1} . \tag{5.3}$$

Expanding $\Theta_1 = 1/2^D$ and Θ_2^2 of (5.1) above (together with (5.2) and (5.3)) in $D = \epsilon$ gives

$$\Theta_1(\infty) + \Theta_2^{(2)}(\infty) = 1 + \epsilon \left(\int_1^2 \frac{\mathrm{d}r}{r} \frac{B(r)}{[1 - B(r)][2 - B(r)]} - \log 2 \right) \tag{5.4}$$

where $B(r) = \frac{2}{\pi} \arccos \frac{r}{2}$.

Numerical evaluation of the integral yields

$$\Theta_1(\infty) + \Theta_2^{(2)}(\infty) = 1 - 0.205\epsilon . \tag{5.5}$$

This equals 0.795 at $\epsilon = 1$, whereas the exact result in one dimension is 0.7476; and 0.590 at $\epsilon = 2$ (to be compared with the simulation result in two dimensions, $\Theta = 0.547$; see [1]).

5.2. *Hypercubes*

We start from (4.2) and write it as

$$\Theta_2^{(2)}(\infty) = \frac{1}{2^D} 2D 2^{D-1} \int_1^2 \mathrm{d}x_1 \int_0^{x_1} \mathrm{d}x_2 \ldots \int_0^{x_1} \mathrm{d}x_D \frac{S_{01}}{[(2a)^D - S_{01}][2(2a)^D - S_{01}]} \tag{5.6}$$

where $2D$ is the number of faces of a cube. The intersection volume for $x_i \geqslant 0, i = 1, \ldots, D$ is

$$S_{01} = (2 - x_1)(2 - x_2) \ldots (2 - x_D) . \tag{5.7}$$

When looking for the ϵ contribution, all the exponents D in (5.6) may be set equal to zero. One can then write the integrand as

$$\frac{1}{1-S_{01}} - \frac{1}{1-S_{01}/2} = \sum_{p=1}^{\infty}\{S_{01}^{p} - (S_{01}/2)^{p}\}. \tag{5.8}$$

Each term in the sum can now be integrated to give

$$\Theta_1(\infty) + \Theta_2^{(2)}(\infty) = 1 + \epsilon\left\{\sum_{p=1}^{\infty}[1-(\tfrac{1}{2})^{p}]\log\frac{2^{p+1}}{2^{p+1}-1} - \log 2\right\} \tag{5.9}$$

or, by numerical evaluation

$$\Theta_1(\infty) + \Theta_2^{(2)}(\infty) = 1 - 0.332\epsilon\,. \tag{5.10}$$

At $\epsilon = 1$ this equals 0.668 (exact value at $D = 1$ is 0.7476), and 0.336 at $\epsilon = 2$ (simulation result: 0.562 [1]).

Except for cubes at $\epsilon = 2$, we see that our approximation (first order in ϵ, plus a maximum of two participating discs or cubes) is surprisingly good.

6. Conclusion

Estimates of the covering fraction $\Theta(\infty)$ in the saturated state of a random sequential adsorption process have so far been based either on numerical simulation or on the judicious extrapolation of an initial-time expansion. Here we have presented a method that gives exact lower bounds for $\Theta(\infty)$, and, more generally, for $\Theta(t)$. The method is an adaptation from previous work [4] on lattice RSA, but takes a very different form for the continuum problems considered here. The numerical values of the lower-order bounds calculated here still fall well below the estimates based on simulation or initial-time extrapolation [3]. The novelty is that they are the first rigorous results and that the method to obtain them is general enough to be applicable to RSA problems of arbitrary type. Future research will be concerned, we think, on the one hand with devising more efficient ways to calculate higher-order terms within the scheme presented here, and on the other hand with exploiting further the flexibility of the basic idea.

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