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## Pair correlation function in random sequential adsorption processes

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**Abstract.** An analytical expression of the pair distribution function is derived for the car-parking problem and for the random sequential adsorption of  $K$ -mers onto a one-dimensional lattice. Both on a lattice and in the continuum limit, super-exponential decay of the distribution function is observed. A comparison of the spatial correlations with those at equilibrium demonstrates the influence of the irreversibility of the RSA process.

### 1. Introduction

Recently, random sequential processes have received a great deal of theoretical and experimental attention [1]. The kinetics of protein [2] and colloid particle adsorption [3] appear to be highly irreversible (surface diffusion and desorption are negligible) and can be suitably described by the random sequential adsorption model (RSA). In this model, particles are placed, one at a time, into a  $D$ -dimensional space. If overlap occurs, the placement is rejected. Eventually, the system reaches a saturation state in which no more particles can be added. The kinetics of this process can be obtained analytically in one dimension [4, 6] and on quasi-one-dimensional ladder lattices [7–9]. In higher dimensions, computer simulation is required because no analytic solution is available.

Most of the theoretical efforts have concentrated on the kinetics or other macroscopic quantities, like the saturation coverage at the jamming limit. However, an experimental determination of the saturation coverage alone is probably not sufficient to establish the irreversible nature of an adsorption process. RSA and equilibrium may be viewed as limiting cases of real adsorption processes. Since the adsorbed phase structures are quite different, a close examination of these structures can help determine the adsorption mechanism. For this purpose, the pair distribution function  $g(r)$ , which already plays a central role in liquid-state physics, is an important quantity in the investigation of RSA models. Moreover,  $g(r)$  can be determined experimentally by monitoring the static structure factor  $S(k)$  via spectroscopic techniques.

Previous analytical studies of spatial correlations in RSA processes [10–15] have been limited mainly to the case of random dimer filling of a line or to the case of the isomorphic model (RSA model with nearest neighbour exclusion). Recently, new results have been obtained for adsorption of particles with mutual nearest-neighbour exclusion on some quasi-one-dimensional ladder lattices [7, 8]. Spatial correlations in more complicated systems have

only been studied numerically. Even for the car-parking problem, Burgos and Bonadeo [16] obtained the pair distribution function by computer simulation.

The purpose of this paper is to derive exact results for one-dimensional substrates. In the second section, using the formal derivation given by Evans *et al* [13], we obtain an exact expression of the pair distribution function for the car-parking problem. The mean-square fluctuations of the total number of particles are also calculated and compared to those of an equilibrium system. In the third section, the method is applied to the one-dimensional lattice versions of this model. We compare, in the last section, the distribution functions with those from equilibrium processes. We show also that the spatial correlations decay much faster in RSA.

## 2. The car-parking problem

We begin by considering an infinite line, assumed empty at  $t = 0$ . Hard rods of length 1 are dropped randomly and sequentially onto the line, and are adsorbed only if they do not overlap previously adsorbed particles. Otherwise, they are rejected. If  $\rho(t)$  denotes the number density of particles on the line at time  $t$ , the kinetics of this process is governed by the equation

$$\frac{d\rho(t)}{dt} = P(l = 1, t) \quad (1)$$

where  $P(l, t)$  is the probability of finding an empty interval of length at least  $l$  [17].

To determine  $P(l, t)$ , note that an empty interval of length  $l \geq 1$  can be destroyed by inserting particles within this interval or by partial overlap to the right or to the left sides of this interval. The time evolution of the probability function  $P(l, t)$  can be expressed in closed form as

$$-\frac{\partial P(l, t)}{\partial t} = (l - 1)P(l, t) + 2 \int_0^1 du P(l + u, t) \quad \text{for } l \geq 1. \quad (2)$$

Using the ansatz

$$P(l, t) = \exp[-(l - 1)t] h^2(t) \quad (3)$$

with the initial condition  $P(l, t = 0) = 1$  yields

$$h(t) = \exp\left(-\int_0^t \frac{1 - e^{-u}}{u} du\right). \quad (4)$$

By inserting (3) in (1),  $\rho(t)$  is easily obtained:

$$\rho(t) = \int_0^t dt' \exp\left(-2 \int_0^{t'} \frac{1 - e^{-u}}{u} du\right). \quad (5)$$

This expression has been derived by Renyi [4] and subsequently rederived by others [6, 18].

To obtain the spatial correlations, we must consider kinetic equations for higher-order distribution functions. Let us denote  $(l + 1)$  as the centre-to-centre distance between two adsorbed particles. The hard core interaction prevents overlap of particles, so the pair distribution function  $g(l + 1) = 0$  for  $(l + 1) < 1$ .  $\rho^2 g(l + 1) dl$  is the probability that centres of two particles located at two given points (1, 2) are separated by the distance  $(l + 1)$ . Between  $t$  and  $t + dt$ , a new pair of particles may be created by the insertion of a particle at point 1 such that a preadsorbed particle exists at point 2, or by the insertion of a

particle at point 2 such that a preadsorbed particle exists at point 1 [19]. The time evolution of the pair distribution function is then given by

$$\frac{\partial \rho^2(t)g(l+1, t)}{\partial t} = 2 Q(l_1 = 1, l, t) \tag{6}$$

where  $Q(l_1, l, t)$  is the probability of finding an empty interval of length at least  $l_1$  at a distance  $l$  (to the right or to the left side) of a preadsorbed particle. The time evolution of  $Q(l_1, l, t)$  can be expressed by considering all possible ways of destruction of available space of length  $l_1$  and all ways to insert a particle at the distance  $l$  of an available space of length  $l_1$ . One obtains, for  $l_1 \geq 1$ ,

$$\begin{aligned} \frac{\partial Q(l_1, l, t)}{\partial t} = & -(l_1 - 1)Q(l_1, l, t) - \int_0^1 du Q(l_1 + u, l, t) \\ & - \int_0^{\text{Min}(1, l)} du Q(l_1 + u, l - u, t) + P(l_1, l, l_2 = 1, t) \end{aligned} \tag{7}$$

where  $P(l_1, l, l_2, t)$  is the probability of finding two empty intervals of length  $l_1$  and  $l_2$  separated by an unspecified interval of length  $l$ .

As all pairs of intervals  $(l_1, l_2)$  separated by the distance  $l$  can only be destroyed when a particle is inserted, the time evolution of  $P(l_1, l, l_2, t)$  can also be written in closed form

$$\begin{aligned} - \frac{\partial P(l_1, l, l_2, t)}{\partial t} = & (l_1 + l_2 - 2)P(l_1, l, l_2, t) + \int_0^1 du (P(l_1 + u, l, l_2, t) \\ & + P(l_1, l, l_2 + u, t)) + \eta \end{aligned} \tag{8}$$

where  $\eta$  is equal to

$$\begin{aligned} \eta = & \int_0^{\text{Min}(1, l)} du (P(l_1 + u, l - u, l_2, t) + P(l_1, l - u, l_2 + u, t)) \\ & + (1 - \text{Min}(1, l))P(l_1 + l_2 + l, t). \end{aligned} \tag{9}$$

Introducing  $P(l_1, l, l_2, t) = h^2(t)p(l, t) \exp[-(l_1 + l_2 - 2)t]$  and  $Q(l_1, l, t) = h(t)q(l, t) \exp[-(l_1 - 1)t]$ , the set of equations can be re-expressed as

$$g(l+1, t) = \frac{2}{\rho^2} \int_0^t dt' h(t') q(l, t') \tag{10}$$

where  $q(l, t)$  satisfies

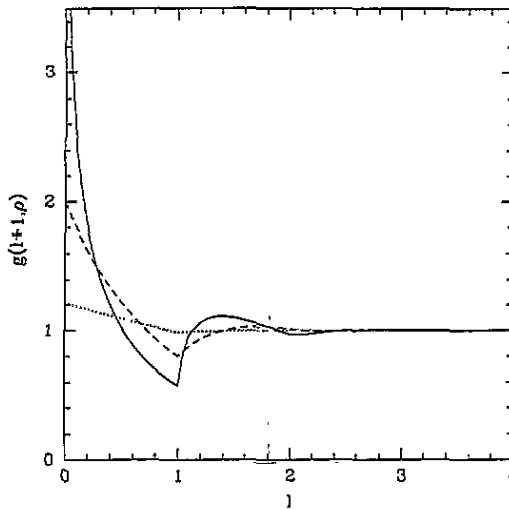
$$\frac{\partial q(l, t)}{\partial t} = h(t)p(l, t) - \int_0^{\text{Min}(1, l)} du e^{-ut} q(l - u, t) \tag{11}$$

and

$$- \frac{\partial p(l, t)}{\partial t} = 2 \int_0^{\text{Min}(1, l)} du e^{-ut} p(l - u, t) + (1 - \text{Min}(1, l)) e^{-(l+1)t}. \tag{12}$$

The solution of (11) and (12) can be obtained for successive intervals ( $[0,1[$ ,  $[1,2[$ , and so on), but the calculation rapidly becomes tedious. As the structure of the distribution function has a relatively short range even at the jamming limit, we present here results only for  $0 \leq l < 2$ , corresponding to the range in which the  $g(l+1, t)$  is significantly structured. After some manipulations, one obtains for  $0 \leq l < 1$ :  $p(l, t) = \exp(-(l+1)t)$  and  $q(l, t) = t h(t) \exp(-lt)$ . Integrating (10) then yields

$$g(l+1, t) = \frac{2}{\rho^2} \int_0^t dt' t' h^2(t') e^{-lt'}. \tag{13}$$



**Figure 1.** Distribution function for the car-parking problem for various values of the density  $\rho$ . The curves from bottom to top correspond to the following sequence:  $\rho = 0.25$ ,  $0.6$  and at the jamming limit ( $\sim 0.74\dots$ ).

Hence, at the jamming limit, when  $l \rightarrow 0^+$ ,  $g(l+1, \infty) \sim -\ln(l)$ : it thus exhibits a logarithmic divergence at contact. Simulation results in two [20] and three dimensions [21] exhibit the same behaviour. Starting from a geometrical analysis of the structure of configurations close to the jamming, Pomeau [22] gives arguments which further support this result.

For  $1 < l \leq 2$ , one finds

$$g(l+1, t) = \frac{2}{\rho^2} \int_0^t dt' t' h^2(t') e^{-lt'} + \frac{2}{\rho^2} \int_0^t dt' h(t') \int_0^{t'} d\tau e^{-\tau} h(\tau) [\tau + sh(\tau)] \times \frac{e^{-(l-1)\tau} - e^{-(l-1)t'}}{t' - \tau}. \quad (14)$$

Figure 1 displays the pair distribution function at three different densities. The minimum of this function is located at  $l = 1$  for all densities, whereas the contact value increase rapidly for densities close to the jamming limit.

We conclude this section by giving an expression of the spatial Laplace transform of the pair distribution and, therefore, a formula for the static-structure factor. For that, we introduce the spatial Laplace transforms  $\tilde{p}(s, t) = \int_0^{+\infty} dl e^{-sl} p(l, t)$  and  $\tilde{q}(s, t) = \int_0^{+\infty} dl e^{-sl} q(l, t)$ . Equations (7) and (8) can be rewritten as

$$-\frac{\partial \tilde{q}(s, t)}{\partial t} = A(s, t) \tilde{q}(s, t) - h(t) \tilde{p}(s, t) \quad (15)$$

and

$$-\frac{\partial \tilde{p}(s, t)}{\partial t} = 2A(s, t) \tilde{p}(s, t) + e^{-t} B(s, t) \quad (16)$$

where

$$A(s, t) = \frac{1 - e^{-(s+t)}}{s+t} \quad (17)$$

and

$$B(s, t) = \frac{1}{s+t} - \frac{1 - e^{-(s+t)}}{(s+t)^2}. \tag{18}$$

Combining (15)–(18), and using the initial conditions  $\tilde{p}(s, 0) = 1/s$  and  $\tilde{q}(s, 0) = 0$ , the spatial Laplace transform of the pair distribution function  $\tilde{g}(s, t) = \int_0^{+\infty} dl e^{-sl} g(l+1, t)$  can be derived:

$$\begin{aligned} \tilde{g}(s, t) = & \frac{1}{\rho^2(t)} \left( \frac{1}{s} \left[ \int_0^t dt_1 \frac{h(t_1)h(t_1+s)}{h(s)} \right]^2 - 2 \int_0^t dt_1 \frac{h(t_1)h(t_1+s)}{h(s)} \int_0^{t_1} dt_2 \frac{h(t_2)h(t_2+s)}{h(s)} \right. \\ & \left. \times \int_0^{t_2} dt_3 \frac{e^{-t_3} h^2(s)}{h^2(t_3+s)} B(s, t_3) \right). \end{aligned} \tag{19}$$

Noting that as  $s \rightarrow 0$ ,  $\tilde{g}(s, t) \rightarrow 1/s$ , and using the Tauberian theorem, we obtain, as expected,  $g(l+1, t) \rightarrow 1$  when  $l \rightarrow +\infty$ . The static structure factor,  $S(k, t)$ , is obtained from (19) by the relation

$$S(k, t) = 1 + 2\rho(t) \operatorname{Re} \left( \lim_{\epsilon \rightarrow 0} \left( \tilde{g}(s, t) e^{-s} - \frac{1}{s} \right)_{s=\epsilon+ik} \right). \tag{20}$$

In figure 2, we plot  $S(k, \rho)$  for various densities ( $\rho \equiv \rho(t)$ ). Compared to the pair distribution function,  $S(k, \rho)$  is more structured. The oscillations results from the short-range contributions of  $g(l+1, \rho)$ .

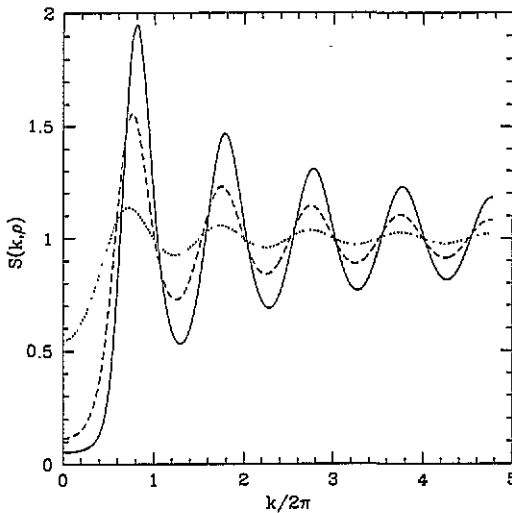


Figure 2. Static structure factor  $S(k, \rho)$  for various densities  $\rho = 0.25, 0.6, 0.74 \dots$

The mean-square fluctuations  $\langle \Delta N^2 \rangle = \langle N^2 \rangle - \langle N \rangle^2$  of the total number,  $N$ , of adsorbed particles is given by the relation

$$\langle \Delta N^2 \rangle = NS(k=0, t). \tag{21}$$

Using (19) and (20) yields

$$\begin{aligned} S(0, t) = & 1 + 2\rho + 2(h^2(t) - 1) - \frac{4}{\rho} \int_0^t dt_1 h^2(t_1) \int_0^{t_1} dt_2 h^2(t_2) \int_0^{t_2} dt_3 e^{-t_3} h^{-2}(t_3) \\ & \times \left( \frac{1}{t_3} - \frac{1 - e^{-t_3}}{t_3^2} \right). \end{aligned} \tag{22}$$

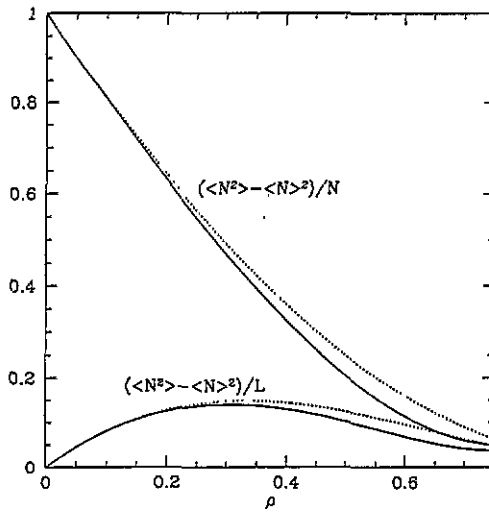


Figure 3. Fluctuations and variance of the total number of particles in equilibrium (broken curve) and RSA (full curve), as functions of density.

At low densities or short times,  $S(k=0, \rho) \simeq 1 - 2\rho$  and  $\langle \Delta N^2 \rangle \simeq N$ , as it is the case at equilibrium. In figure 3, we plot  $\langle \Delta N^2 \rangle / N$  and  $\langle \Delta N^2 \rangle / L$  (where  $L$  is the size of the system) as functions of the density. The curves corresponding to the equilibrium system are also plotted. Fluctuations in RSA are slightly less important than in equilibrium at a given density.  $S(0, \rho(t))$  goes to an asymptotic value around  $5 \times 10^{-2}$ . Note that  $\langle \Delta N^2 \rangle / N$  is a decreasing function, whereas  $\langle \Delta N^2 \rangle / L$  exhibits a maximum.

### 3. Pair distribution function for the discrete $K$ -mer case

The car-parking problem presented above is the scaling limit of the adsorption of  $K$ -mers onto a one-dimensional lattice when  $K \rightarrow \infty$ . The above method can be applied to the lattice models which relate physically to problems in polymer chemistry [1, 5, 6]. To simplify the kinetic equations and to recover the continuum limit easily, we take a rescaled deposition rate per  $K$ -mer equal to  $1/K$  and we introduce the notation  $z = e^{-t/K}$ . We consider the probability  $P_K(k, z)$  of finding a sequence of at least  $k$  vacant sites on the lattice. The rate equation for  $P_K(k, z)$  has a closed form

$$z \frac{\partial P_K(k, z)}{\partial z} = 2 \sum_{n=1}^{K-1} P_K(k+n, z) + (k-K+1)P_K(k, z) \quad \text{for } k \geq K. \quad (23)$$

Integrating (23) yields

$$P_K(k, z) = z^{k-K+1} h_K^2(z) \quad (24)$$

where, for  $K \geq 2$ ,  $h_K(z)$  is given by

$$h_K(z) = \exp \left( - \int_0^{K(1-z)} \frac{1 - (1-u/K)^{K-1}}{u} du \right) \quad (25)$$

and  $h_1(z) = 1$  for  $K = 1$ . The fraction of covered sites,  $\rho_K(z)$ , can be derived from  $P_K(k, z)$ :

$$z \frac{\partial \rho_K(z)}{\partial z} = -K P_K(K, z). \quad (26)$$

Following on integration of (26) and a change of the variable  $z$  back to  $t$ , the fraction of covered sites at time  $t$  is obtained as

$$\rho_K(t) = \int_0^{K(1-\exp(-t/K))} du \exp\left(-2 \int_0^u \frac{1 - (1 - v/K)^{K-1}}{v} dv\right). \tag{27}$$

It is easy to verify that explicit integration in (25) can only be done for  $K = 1$  ( $\rho_1(t) = 1 - \exp(-t)$ ) and for  $K = 2$  ( $\rho_2(t) = 1 - \exp(-2 + 2\exp(-t/2))$ ). However, the continuum case corresponding to  $K \rightarrow +\infty$  may be readily recovered from (26) [6]. Furthermore, Bartelt *et al* [23] have recently obtained a systematic derivation of the  $1/K$ -Taylor expansion for the jamming coverage.

To obtain the pair distribution function, we define  $Q_K(k_1, k, t)$  as the probability of finding a sequence of  $k_1$  vacant sites separated by  $k$  (unspecified) sites from a preadsorbed  $K$ -mer and  $P_K(k_1, k, k_2, t)$  as the probability of finding a sequence of  $k_1$  vacant sites separated by another sequence of  $k$  unspecified sites from a sequence of  $k_2$  vacant sites. We can then write a set of closed equations for the pair distribution function  $g_K(k + K, z)$ :

$$g_K(k + K, z) = \frac{2K}{\rho_K^2} \int_z^1 du \frac{Q_K(K, k, u)}{u} \tag{28}$$

where  $Q_K(k_1, k, z)$  satisfies

$$z \frac{\partial Q_K(k_1, k, z)}{\partial z} = \sum_{n=1}^{K-1} Q_K(k_1 + n, k, z) + \sum_{n=1}^{\text{Min}(k, K-1)} Q_K(k_1 + n, k - n, z) + (k_1 - K + 1)Q_K(k_1, k, z) - K P_K(k_1, k, K, z) \tag{29}$$

and  $P_K(k_1, k, k_2, z)$  obeys

$$z \frac{\partial P_K(k_1, k, k_2, z)}{\partial z} = \sum_{n=1}^{K-1} [P_K(k_1 + n, k, k_2, z) + P_K(k_1, k, k_2 + n, z)] + (k_1 + k_2 - 2K + 2)P_K(k_1, k, k_2, z) + \sum_{n=1}^{\text{Min}(k, K-1)} [P_K(k_1 + n, k - n, k_2, z) + P_K(k_1, k - n, k_2 + n, z)] + (K - 1 - \text{Min}(k, K - 1))P_K(k_1 + k + k_2, z). \tag{30}$$

Introducing the functions  $P_K(k_1, k, k_2, z) = z^{k_1+k_2+2-2K} h_K^2(z) p_K(k, z)$  and  $Q_K(k_1, k, z) = z^{k_1+1-K} h_K(z) q_K(k, z)$ , equations (28)–(30) can be rewritten as

$$g_K(k + K, z) = \frac{2K}{\rho_K^2} \int_z^1 du h_K(u) q_K(k, u) \tag{31}$$

$$z \frac{\partial q_K(k, z)}{\partial z} = \sum_{n=1}^{\text{Min}(k, K-1)} z^n q_K(k - n, z) - K z h_K(z) p_K(k, z) \tag{32}$$

and

$$z \frac{\partial p_K(k, z)}{\partial z} = 2 \sum_{n=1}^{\text{Min}(k, K-1)} z^n p_K(k - n, z) + (K - 1 - \text{Min}(k, K - 1))z^{k+K-1}. \tag{33}$$

As for continuum case, equations (32) and (33) can be solved for successive intervals of  $k$ . Therefore, for  $0 \leq k < K$ , one finds that  $p_K(k, z) = z^{k+K-1}$ ,  $q_K(k, z) = K(1 - z)h_K(z)z^k$ , and that  $g_K(k + K, t)$  is given by

$$g_K(k + K, t) = \frac{2}{\rho_K^2} \int_0^{K(1-\exp(-t/K))} du u \left[1 - \frac{u}{K}\right]^k \exp\left(-2 \int_0^u \frac{1 - (1 - v/K)^{K-1}}{v} dv\right). \tag{34}$$



Following algebraic manipulations, one obtains, for  $K \leq k < 2K$ ,

$$\begin{aligned}
 g_K(k+K, t) &= \frac{2}{\rho_K^2} \int_0^{K(1-\exp(-t/K))} du \exp\left(-\int_0^u \frac{1-(1-v/K)^{K-1}}{v} dv\right) \\
 &\times \int_0^u dv \frac{(1-u/K)^{k-K+1} - (1-v/K)^{k-K+1}}{u-v} \\
 &\times \exp\left(-\int_0^v \frac{1-(1-w/K)^{K-1}}{w} dw\right) \\
 &\times (1-v/K)^{K-1} \left[ v + \frac{(1-v/K)^{-K-1} - (1-v/K)^K}{2-1/K} \right]. \quad (35)
 \end{aligned}$$

An expression of the pair distribution function can be obtained by taking discrete space Laplace transforms. By defining the generating functions  $\bar{p}_K(x, z) = \sum_{k=0}^{+\infty} x^k p_K(k, z)$  and  $\bar{q}_K(x, z) = \sum_{k=0}^{+\infty} x^k q_K(k, z)$ , (32) and (33) can be rewritten as

$$z \frac{\partial \bar{q}_K(x, z)}{\partial z} = A_K(x, z) \bar{q}_K(x, z) - zK h_K(z) \bar{p}_K(x, z) \quad (36)$$

and

$$z \frac{\partial \bar{p}_K(x, z)}{\partial z} = 2A_K(z, t) \bar{p}_K(x, z) + z^{k-1} B_K(x, z) \quad (37)$$

where

$$A_K(x, z) = \sum_{n=1}^{K-1} (xz)^{n-1} \quad (38)$$

and

$$B_K(x, z) = \sum_{n=1}^{K-1} (K-1-n)(xz)^{n-1}. \quad (39)$$

Combining (36)–(39), and using the initial conditions  $\bar{p}(x, z=1) = 1/(1-x)$  and  $\bar{q}(x, z=1) = 0$ , the generating function of the pair distribution function  $\bar{g}_K(x, z) = \sum_{k=0}^{+\infty} x^k g_K(k+K, z)$  can be derived:

$$\begin{aligned}
 \bar{g}_K(x, z) &= \frac{K^2}{\rho_K^2(z)} \left( \frac{1}{1-x} \left[ \int_z^1 du \frac{h_K(u)h_K(xu)}{h_K(x)} \right]^2 \right. \\
 &\quad \left. - 2 \int_z^1 du \frac{h_K(u)h_K(xu)}{h_K(x)} \int_u^1 dv \frac{h_K(v)h_K(xv)}{h_K(x)} \int_v^1 dw \frac{w^{k-2}h_K^2(x)}{h_K^2(xw)} B_K(w, z) \right). \quad (40)
 \end{aligned}$$

In order to obtain  $g_K(k, t)$ , the inverse discrete Laplace transform of expression (38) must be computed. Figure 4 displays the pair distribution function for various values of  $K$ . If we introduce  $l = (k+1)/K$ , the curve  $g_K(l, t)$ , when plotted as a function of  $l$ , rapidly converges towards the continuum case for large  $K$  (if  $l \geq 1$ ).

For lattices, the static structure factor  $S_K(q, z)$  is defined as

$$S_K(q, z) = 1 + \frac{\rho_K}{K} \sum_{k=-\infty}^{k=+\infty} e^{iqk} [g_K(k, z) - 1]. \quad (41)$$

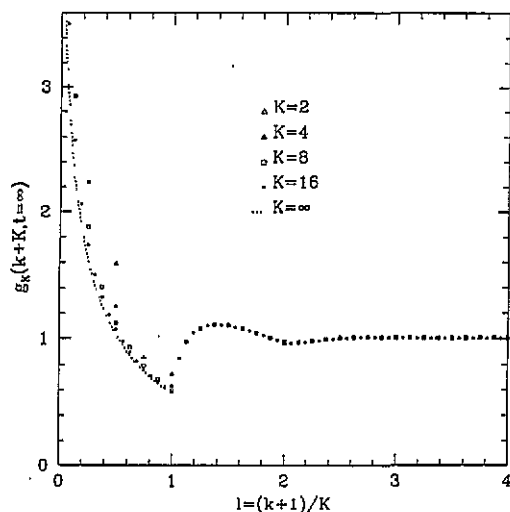


Figure 4. Distribution function for  $K$ -mers random sequential addition at the jamming limit. The curves correspond to the following sequence:  $K = 2, 4, 8, 16$ . The broken curve corresponds to the continuum limit.

If we set  $g_K(k, z) = g_K(-k, z)$  and note that  $g_K(k, z) = 0$  if  $k < K$ , the static structure factor can be re-expressed as

$$S_K(q, z) = 1 - \frac{\rho_K}{K} + \frac{2\rho_K}{K} \operatorname{Re} \lim_{\epsilon \rightarrow 0^+} \left( x^K \tilde{g}_K(x, z) - \frac{x}{1-x} \right)_{x=e^{iq-\epsilon}} \quad (42)$$

The mean fluctuation  $\langle \Delta N^2 \rangle$  of the total number of particles is obviously related to  $S_K(q, z)$  by the relation  $\langle \Delta N^2 \rangle = N S_K(q = 0, z)$ .

For  $K = 2$ , there exists explicit expressions for the coverage, the pair distribution function  $g_2(k + 2, t)$ , the static-structure factor and the fluctuations of number of particles. Inserting (25) in (40) for  $K = 2$  yields

$$\rho_2^2 \tilde{g}_2(x, z) = \frac{2}{1-x^2} + \frac{2 \exp(-2(1+x)(1-z))}{x(1-x^2)} - \frac{2 \exp(-2(1-z))}{x(1-x)} \quad (43)$$

Expanding in power of  $x$ , the pair distribution function for dimers is obtained as

$$\rho_2^2 g_2(k + 2, t) - \rho_2^2 = -2 e^{-2(1-e^{-t/2})} \sum_{n=0}^{\infty} \frac{(-2(1-e^{-t/2}))^{2n+k+3}}{(2n+k+3)!} \quad (44)$$

Exploiting the mapping between the random dimer filling and the adsorption of points with nearest-neighbour exclusions [12], and dividing the density by a factor of two, we recover the pair correlation for random sequential adsorption of particles with nearest neighbour exclusion [12, 14, 18]. Using expressions (42) and (43), we obtain the same  $S_2(q, z)$  as previously derived by others [12, 14]. (Note that Monthus and Hilhorst [14] use a different definition for the static structure factor.)

We pay particular attention to the mean-square fluctuation of particles:

$$\frac{\langle \Delta N^2 \rangle}{N} = S_2(0, z) = \frac{2(1-z) e^{-4(1-z)}}{1 - e^{-2(1-z)}} \quad (45)$$

or

$$\frac{\langle \Delta N^2 \rangle}{L} = \frac{\rho_2}{2} S_2(0, z) = 2(1-z) e^{-4(1-z)} \quad (46)$$

Since the number of sites occupied by a dimer is two, the mean fluctuation of occupied sites is equal to  $4\langle\Delta N^2\rangle$ . Moreover, since the total number of vacant and occupied sites is conserved, their fluctuations are equal. We recover then the result of Cohen and Reiss [24] concerning the variance in the number of vacant sites in the RSA of dimers. Finally, expression (46) is equivalent to the result given by Pedersen and Hemmer [15] for particles with nearest-neighbour exclusion.

#### 4. Discussion

We now proceed to a more detailed comparison of configurations of hard rods either generated at equilibrium or by RSA. The distribution function for an equilibrium system of hard rods of length unity has been derived [25] and is given by

$$g_{\text{eq}}(l+1, \rho) = \frac{1}{\rho} \sum_m \frac{(l+1-m)^{m-1}}{(m-1)!(1/\rho-1)^m} \exp\left(-\frac{l+1-m}{1/\rho-1}\right) \quad \text{when } l > 0 \quad (47)$$

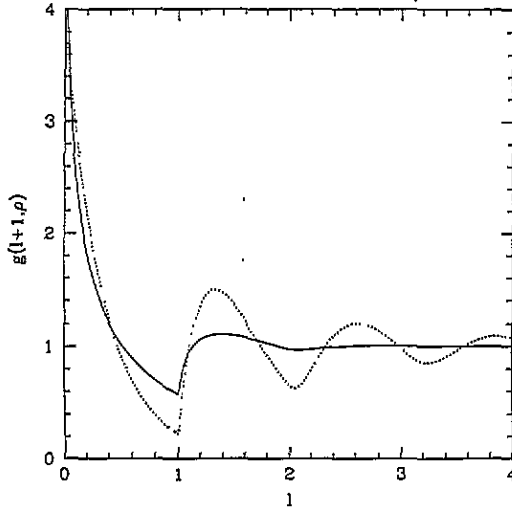


Figure 5. Comparison between the equilibrium (broken curve) and RSA (full curve) pair distribution functions at  $\rho = 0.74$ .

where for a given  $l+1$ , the sum is extended over those terms for which  $l+1-m$  remains positive. Using results in section 2, we plot in figure 5 both distribution functions for the density of 0.74 (i.e. the jamming limit of the car-parking problem). Larger differences appear between equilibrium and RSA when the density increases. A density expansion of the pair correlation function shows that the first-order coefficients already differ in these two cases. At high density,  $g_{\text{eq}}(l+1, \rho)$  displays additional large oscillations, indicating the increasing range of structure in the liquid. This comparatively large correlated region extends over a number of particles approximately equal to  $1/(1-\rho)^2$ , i.e. around 16 at  $\rho = 0.74$ . In RSA, the correlation length is small, even close to the jamming limit:  $g(l+1, \rho)$  is practically flat for  $l > 2$ . Moreover, at large distances,  $g_{\text{eq}}(l+1, \rho)$  goes to 1 exponentially [26, 27]. In RSA, at large distances, one can obtain the asymptotic approach as follows. When  $l \rightarrow \infty$ , (10)–(12) can be solved and one obtains that  $p(l, t) \rightarrow h^2(t)$ ,  $q(l, t) \rightarrow h(t)\rho(t)$ , and

$g(l + 1, t) \rightarrow 1$ . Inserting  $p(l, t) = h^2(t) + e^{-lt} \mu(l)$  and  $q(l, t) = h(t)\rho(t) + e^{-lt} \nu(l, t)$  in (10)–(12), one obtains

$$\mu(l) = \frac{2}{l} \int_{l-1}^l \mu(u) du \tag{48}$$

and

$$\frac{\partial \nu(l, t)}{\partial t} - l\nu(l, t) = h(t)\mu(l) - \int_{l-1}^l \nu(u, t) du. \tag{49}$$

For large  $l$ , we get, from (48),  $\mu(l) \propto 2^l (\ln l)^{-l} / \Gamma(l)$ , where  $\Gamma$  denotes the gamma function. Equation (49) gives the leading term  $\nu(l, t) \simeq -2h(t) \mu(l)$ . By integrating (10), the decay of the distribution function is then given by

$$g(l + 1, \rho) - 1 \propto \frac{1}{\Gamma(l + 1)} \left( \frac{2}{\ln l} \right)^l. \tag{50}$$

Hence, faster-than-exponential decay is observed for  $g(l + 1, \rho)$ . This decay is even stronger for the car-parking problem than for lattice RSA, which has been derived previously as a  $1/(l + 1)!$  law for dimers [14, 15], and, more generally, for  $K$ -mers [13].

In summary, the pair correlation function in RSA is a short-range function at any density, characterized by a logarithmic divergence at contact in the jamming limit. Contrary to equilibrium, the pair distribution function of the one-dimensional problem contains informations valid in higher dimensions as well. Brosilow *et al* [28] studied deposition of aligned squares on a plane, and it comes out that the shape of our  $g(l + 1, \rho)$  at the jamming limit (plotted in figure 1) is similar to the one obtained numerically by them for the squares along the horizontal direction. A possible reason for this comes from the fact that both systems are composed of oriented objects. Simulation results for the RSA of disks [29] on a plane show a less ordered structure.

Typically, the liquid state is modelled via a set of approximate integral equations for the pair distribution function, derived from a hierarchy of equations, in which the higher distribution functions are approximated by factorization. It is tempting to investigate these functions in RSA as well [19]. In particular, the Percus–Yevick equation relies on the factorization of the triplet function,  $g(l + 1, l' + 1, \rho) = g(l + 1, \rho)g(l' + 1, \rho)$ , an exact result in one dimension. Unfortunately, in RSA, this relation does not hold even in one dimension. However, using the method developed in section 2, one can derive the triplet nearest-neighbour distribution function. For  $0 < l < 1$  and  $0 < l' < 1$ , the triplet distribution function is equal to

$$g(l + 1, l' + 1, t) = \frac{1}{\rho^3(t)} \left( \int_0^t dt_1 t_1^2 h^2(t_1) e^{-(l+l')t_1} + \int_0^t dt_1 h(t_1) \times \int_0^{t_1} dt_2 e^{-t_2} h(t_2) [t_2 + sh(t_2)] [e^{-(l+l')t_2} + e^{-(l'+l_2)t_2}] \right) \tag{51}$$

which clearly differs from  $g(l + 1, t)g(l' + 1, t)$ . An alternative derivation of (51) can be done by using the *gap-particle-gap* distribution function [30]. The RSA pair distribution function has a short-range structure, but the multi-particle correlations have a highly non-trivial behaviour which obscures the derivation of approximate integral equations.

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