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Density fluctuations of assemblies of irreversibly deposited particles on solid surfaces

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For general irreversible deposition processes, a relation between the variance σ^2 of the number of deposited particles on subsystems out of a large surface and the available surface function Φ is obtained. This relation is based on a mean field assumption and follows the resolution of a master equation system. It is valid at low to intermediate values of the surface coverage θ as shown by comparison with exact results and with numerical simulations for special deposition models. In the low coverage limit, if the available surface function is written as a series expansion of the coverage θ, whose first nontrivial term varies as θ^k, the reduced variance has a similar expansion. However, the prefactor of θ^k derived in this article is in general different in both series expansions. This result has also been obtained by a rigorous argument based on the evolution of the k-particle distribution function with the coverage. © *1997 American Institute of Physics.* [S0021-9606(97)50830-0]

I. INTRODUCTION

Fluctuations play a great role in physics and many studies in statistical mechanics have been devoted to their understanding. Density fluctuations in systems at equilibrium are, for example, directly related to the compressibility of the system. The formation of a liquid droplet in a supersaturated gas in homogeneous nucleation is also a consequence of a large density fluctuation. Density fluctuations are also responsible for the scattering of light in liquids, and their study has played a central role in the understanding of critical phenomena. Recently, it has been realized that the study of fluctuations is not only of interest for systems at equilibrium, but that it also contains valuable information on irreversible deposition processes.[1–8] Such processes are of general interest to adsorption phenomena, sedimentation, filtration, etc.

In order to describe these irreversible deposition processes in different physical circumstances, several sequential deposition models have been investigated. These models are characterized by the two following properties: (1) particles arrive randomly and sequentially at the vicinity of the adsorbing surface; and (2) each particle arriving near the surface can be irreversibly adsorbed or rejected with a probability depending on the local distribution of previously adsorbed particles. For very large surfaces, the adsorption kinetics derived from these models is related to the available surface function, $\Phi(\theta)$, which represents the probability that a particle arriving over the surface will adsorb when the value of the coverage is θ. However, in order to describe real finite surfaces, it is necessary to take into account the fluctuations of the coverage or of the number density.

Three approaches to investigate density fluctuations for irreversible deposition processes have been proposed:

(i) In a first approach,[1] one describes the evolution of a small system S (a subsystem) which is part of a much larger one, R, by a master equation. In this approach, the evolution of the probability $q(n+1, N+1)$ to find $n+1$ particles in the system S, when $N+1$ particles are deposited on R, is expressed as a function of the probabilities $q(n, N)$ and $q(n+1,N)$ through the conditional probabilities $p(n+1,N+1|n,N)$ and $p(n+1,N+1|n+1,N)$ by the relation:

$$q(n+1,N+1)=q(n,N)p(n+1,N+1|n,N)+q(n+1,N)p(n+1,N+1|n+1,N). \tag{1}$$

These latter represent, respectively, the conditional probabilities that when n (resp. $n+1$) particles are deposited on S, and N particles on R, there will be $n+1$ particles adsorbed on S after the $(N+1)$th particle has adsorbed on R. These conditional probabilities are expressed in terms of the available surface function $\Phi(\theta)$. More specifically, $p(n+1,N+1|n,N)$ is given by

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$$p(n+1,N+1|n,N)=\frac{a\Phi(\theta_a)}{A\Phi(\theta)}, \tag{2}$$

where a (resp. A) is the area of the system S (resp. R) and θ_a (resp. θ) is the coverage of the system S (resp. R). The particles are assumed to be of unit area, therefore the coverages coincide with the number densities, $\theta=N/A$ and $\theta_a=n/a$. Expression (2) constitutes a mean field (mf) approximation because it is assumed that the deposition probability is only a function of the coverage of the system, even for the small system S. This is certainly valid for systems of large area, but not for smaller systems, where this probability becomes an explicit function of the ''microscopic'' configuration. For the case of a random sequential adsorption (RSA) procedure, the master Eq. (1), assuming relation (2), has been solved by a one-dimensional computer simulation, described in detail in Ref. 1. The results have been compared directly to those obtained from simulations of the deposition process, showing that this approach underestimates the density fluctuations, especially at coverages larger than 20%. This effect has been attributed to the fact that the fluctuations of the available surface function at a given coverage, with the different particle configurations on the surface, are neglected. Indeed, this effect becomes important once the exclusion surfaces associated with the particles overlap. Then, Φ is no longer uniquely determined by θ.

(ii) A second approach[3] is based on a combinatorial calculation of the number of possibilities that exist to deposit n particles on the subsystem S and N particles on R. In order to be able to perform the analytical calculation, the same mean field approximation as described above is introduced. It leads to the probability $p(n,\langle n\rangle)$ to observe n particles in the subsystem when the expected mean number of adsorbed particles is $\langle n\rangle$. If $\Phi(\theta)$ is expressed as a power series of the coverage, i.e., $\Phi(\theta)=1-B_k\theta^k+0(\theta^{k+1})$, one gets for the reduced variance the expression

$$\frac{\sigma^2}{\langle n\rangle}=1-kB_k\theta^k+0(\theta^{k+1}). \tag{3}$$

(i) A third approach based on the general rigorous expression:[9]

$$\frac{\sigma^2}{\langle n\rangle}=1+\rho\int_0^\infty [g(r)-1]2\pi r\,dr, \tag{4}$$

which relates the reduced variance $\sigma^2/\langle n\rangle$ to the radial distribution function $g(r)$ of the particles on the surface,[5,6] at a given density ρ of adsorbed particles. This expression is only valid for systems that are large enough so that border effects can be neglected.[2] For adsorption models on two-dimensional surfaces, usually only the first terms of the virial expansion of $g(r)$ are known. Therefore this approach allows only the calculation of the reduced variance up to the first nonvanishing order in the density, and is thus limited to small coverages. By evaluating the changes in the integral of the radial distribution function after the deposition of new particles on the surface, it was shown that the reduced variance behaves as

$$\frac{\sigma^2}{\langle n\rangle}=1-B_k\theta^k+0(\theta^{k+1}). \tag{5}$$

For small surface coverages it behaves, thus, in the same way as the available surface function $\Phi(\theta)$. Note that k corresponds to the minimum number of particles deposited on the surface that are necessary to prevent the deposition of a new one. It must be noticed that this expression is only in accordance with expression (3) when $k=1$, which corresponds to the RSA case.

A careful analysis of the procedures leading to these results reveals that they are not entirely correct. Indeed, in Ref. 5, in order to evaluate $g(r)$, one takes each adsorbed particle as a ''center particle'' and determines the number of its neighbors at a given distance r. Once adsorbing a new particle on the surface, the number of the neighbors changes. However, one should also take the new adsorbing particle as a ''center particle.'' This would contribute an additional modification of the radial distribution function after adsorption. On the other hand, the combinatorial calculation of Ref. 3 does not take into account the fact that the probability for a new particle to be adsorbed in a subsystem S depends not only on the local coverage θ_a, but also on the coverage of the entire surface, θ, as shown in Eq. (2). As a consequence, this approach yields correctly only the one-particle contribution to the reduced variance, i.e., Eq. (3) is only correct at small coverages and for $k=1$.

In the present paper we reanalyze the problem of the density fluctuations by using the approach (i). We will first (Sec. II) develop an analytical procedure which allows us to solve the master equation for large systems over the entire coverage range. The mean field approximation already discussed will be used. The main result of this approach is that the reduced variance of the density is a function, within our approximations, of the available surface function Φ only, over the entire coverage range, and not only at low coverage. This new result explains why systems with similar available surface functions also behave identically in regards to the reduced variance $\sigma^2/\langle n\rangle$, in accordance with the experimental observations. The evaluation of the reduced variance through the master equation, over the entire coverage range, will also be compared to theoretical predictions concerning the irreversible deposition on a line, for which exact solutions exist.[4,10] From this analysis it will be shown that, if the available surface function $\Phi(\theta)$ behaves, at low coverage, as $\Phi(\theta)=1-B_k\theta^k+0(\theta^{k+1})$, then the reduced variance of the particle number distribution behaves as $1-[2k/(k+1)]B_k\theta^k+0(\theta^{k+1})$ instead of $1-B_k\theta^k+0(\theta^{k+1})$. This finding, for low coverages, will also be obtained using the rigorous method (iii), in which all the sources of change of the radial distribution function $g(r)$, when a new particle is deposited on the surface, will now be taken into account (Sec. III).

II. MASTER EQUATION APPROACH

In this section we will obtain an analytical relation between the variance of the particle number distribution, σ^2, and the available surface function, $\Phi(\theta)$, by using the master equation (1) for sufficiently large surfaces. This equation is based on a mean field approximation which neglects the fact that configurations of adsorbed particles, corresponding to the same coverage, can have different available surface functions. We expect this hypothesis to be fairly correct as long as the jamming limit regime is not reached. Nevertheless, its validity can be confirmed by computer simulations only, unless we deal with the one-dimensional RSA and ballistic deposition (BD) models, where exact results can be obtained.

Using (2) and taking into account that $p(n,N+1|n,N)=1-p(n+1,N+1|n,N)$, the master equation (1) can be rewritten as

$$q(n+1,N+1)-q(n+1,N)=\frac{a}{A\Phi(\theta)}\left[q(n,N)\Phi\left(\frac{n}{a}\right)-q(n+1,N)\Phi\left(\frac{n+1}{a}\right)\right]. \quad (6)$$

The system R being assumed to be very large, the addition of one particle produces an infinitesimal change of its coverage. The master equation can then be written in differential form:

$$\frac{\partial q(n,\theta)}{\partial\theta}=\frac{a}{\Phi(\theta)}\left[q(n-1,\theta)\Phi\left(\frac{(n-1)}{a}\right)-q(n,\theta)\Phi\left(\frac{n}{a}\right)\right], \quad (7)$$

where θ corresponds to the coverage of the large system. Note that the area covered by one particle is taken as unity without loss of generality.

When the subsystem S is also large (but much smaller than R), the probability distribution $q(n,\theta)$ is expected to be strongly peaked around the average value, $\langle n\rangle$ (proportional to a), and to have a width of order $a^{1/2}$. In these circumstances it is possible to make a large-system expansion of the master equation (7).[11] The leading terms of that expansion yield a deterministic evolution equation for the average particle number, $\langle n\rangle$, and a linear Fokker–Planck equation for the distribution of the fluctuations. Consequently, in this limit the probability distribution becomes Gaussian and is completely characterized by its first and second moments.

The first moment of $q(n,\theta)$ gives the mean particle number, $\langle n\rangle=\Sigma_{n>0}nq(n,\theta)$, and its evolution equation is easily obtained from (7):

$$\frac{d\langle n\rangle}{d\theta}=\frac{a}{\Phi(\theta)}\sum_{n\geqslant 0}q(n,\theta)\Phi\left(\frac{n}{a}\right)\equiv\frac{a}{\Phi(\theta)}\left\langle\Phi\left(\frac{n}{a}\right)\right\rangle. \quad (8)$$

In the same way, for the second moment one obtains

$$\frac{d\langle n^2\rangle}{d\theta}=\frac{a}{\Phi(\theta)}\left\langle(2n+1)\Phi\left(\frac{n}{a}\right)\right\rangle. \quad (9)$$

Given that $\Phi(\theta)$ is in general a nonlinear function, these equations cannot be solved analytically. However, if the area a is large enough, the fluctuations of n will be relatively small, and only values of n near $\langle n\rangle$ will contribute to the averages. In that case, one can expand $\Phi(n/a)$ as a Taylor series around $\langle n\rangle/a$:

$$\Phi\left(\frac{n}{a}\right)=\Phi\left(\frac{\langle n\rangle}{a}\right)+\left(\frac{n-\langle n\rangle}{a}\right)\Phi'\left(\frac{\langle n\rangle}{a}\right)+0\left[\left(\frac{n-\langle n\rangle}{a}\right)^2\right], \quad (10)$$

where $\Phi'(x)$ denotes the derivative of $\Phi(x)$. Using this expansion in (8) one obtains the equation for the evolution of the mean particle number:

$$\frac{1}{a}\frac{d\langle n\rangle}{d\theta}=\frac{1}{\Phi(\theta)}\Phi\left(\frac{\langle n\rangle}{a}\right)+0\left(\frac{1}{a}\right). \quad (11)$$

The obvious solution, neglecting finite size effects, is $\langle n\rangle/a=\theta$, and expresses the fact that the mean coverage of the subsystem S is the same as the coverage of the large system R. In the same way, inserting the expansion (10) into equation (9), yields an equation for $\langle n^2\rangle$. From that equation, one can write the evolution equation for the variance $\sigma^2=\langle n^2\rangle-\langle n\rangle^2$:

$$\frac{1}{a}\frac{d\sigma^2}{d\theta}=1+2\frac{\Phi'(\theta)}{\Phi(\theta)}\frac{\sigma^2}{a}+0\left(\frac{1}{a}\right). \quad (12)$$

This equation gives the relation between the variance of the adsorbed particle number and the available surface function. It is applicable, in principle, to all adsorption models whose kinetics can be described as a Markov process. Its validity is limited by the mean field assumption implied in the master equation (1), which fails near the jamming limit, while leading to good results for low and intermediate coverages.

If the available surface function is of the form $\Phi(\theta)=1-B_k\theta^k+0(\theta^{k+1})$, using (12) leads to the expansion for the reduced variance:

$$\frac{\sigma^2}{\langle n\rangle}=1-\frac{2k}{k+1}B_k\theta^k+0(\theta^{k+1}). \quad (13)$$

In the next section we will verify that this result is valid in general and does not depend on the mean field assumption.

For the RSA model in two dimensions, two terms of the development of σ^2 are known.[2] Introducing in (12) the first two terms of the available surface function, $\Phi(\theta)=1-B_1\theta+B_2\theta^2+0(\theta^3)$, it is easy to obtain the corresponding expansion of $\sigma^2/\langle n\rangle$:

$$\frac{\sigma^2}{\langle n\rangle}=1-B_1\theta+\frac{4}{3}B_2\theta^2+0(\theta^3). \quad (14)$$

This expression agrees with the results of Ref. 2, obtained from a virial expansion. Therefore, at least in this case, the results derived from the mean field approach are valid beyond the first order terms. For general values of the coverage, the solution of the first order differential equation (12), satisfying the proper initial condition for an empty surface, $\sigma^2=0$ for $\theta=0$, is

$$\frac{\sigma^2}{\langle n\rangle}=\frac{\Phi^2(\theta)}{\theta}\int_0^\theta\frac{d\theta'}{\Phi^2(\theta')}, \quad (15)$$

where $\langle n\rangle/a=\theta$ has also been used. Therefore, if $\Phi(\theta)$ is known, the variance of the number of deposited particles on subsystems out of a large surface can be obtained by a simple quadrature.

For the one-dimensional RSA and BD models, the exact expressions of the available surface function $\Phi(\theta)$ and of the reduced variance are known.[10,12,13] It is therefore possible to integrate the relation (15) and to compare the result to the exact reduced variance (Fig. 1). One can see that the mean field approximation gives excellent results for values of the coverage up to 50% of the jamming value. Near jamming the mean field approximation predicts that the reduced variance $\sigma^2/\langle n\rangle$ approaches 0, while the exact expression approaches a nonzero value (Sec. IV).

No exact results exist for two-dimensional deposition models. In order to check the validity of (15), one has to compare it with results obtained from computer simulations, the available surface function being itself determined from such simulations. Figure 2(a) shows the results corresponding to the RSA model. The expression of $\sigma^2/\langle n\rangle$ has been taken from Ref. 2, where it was derived on the basis of both theoretical arguments and numerical simulations. The expression of $\Phi(\theta)$, which spans the entire range of coverage, from 0 up to 0.547, was taken from Ref. 14. As can be seen, the results are qualitatively similar to those of the one-dimensional model. In the case of the BD model [Fig. 2(b)], we have used the ballistic deposition algorithm[15] to cover surfaces up to coverages near saturation. From these simulations, we derived as well $\Phi(\theta)$ as $\sigma^2/\langle n\rangle$. As to the available surface function, it can be expressed as a polynomial of degree five, namely $\Phi(\theta)=1-B_3\theta^3+B_4\theta^4-B_5\theta^5$, with B_3 fixed to its theoretical value[16] $B_3=9.94978$, B_4 and B_5 being free parameters ($B_4=13.8113$, $B_5=7.805\,15$). Furthermore, $\sigma^2/\langle n\rangle$ has been represented by $\sigma^2/\langle n\rangle=1-C_3\theta^3+C_4\theta^4-C_5\theta^5$, with $C_3=3B_3/2$ according to Eq. (14), $C_4=21.7386$, and $C_5=6.553\,83$. The quality of the agreement between our approximation and the simulation results is comparable to that obtained in the one-dimensional case.

III. DISTRIBUTION FUNCTION APPROACH

In this section we will derive the low density expression (14) of the reduced variance of the particle number distribution, following an approach using the distribution functions characterizing the system of particles deposited on the surface. We will follow closely a method developed in Ref. 5 and also take over the notations of this article.

Let $r^{(k)}(1\ldots k)$ represent the generic distribution function of order k,[17] and $1\ldots k$ be a shorthand notation for the position vectors $\mathbf{r}_1\ldots\mathbf{r}_k$. If at least k particles have to be present in order to exclude the adsorption of a new particle, the available surface function $\Phi(\rho)$ is given by

$$\Phi(\rho)=1-\frac{1}{k!}\frac{1}{A}\int\ldots\int\rho^{(k)}(1\ldots k)A_{\mathrm{ex}}(1\ldots k)d1\ldots dk+0(\rho^{k+1}),\tag{16}$$

where r represents the density of adsorbed particles on the system of area A. $A_{\mathrm{ex}}(1\ldots k)$ corresponds to the area ex-

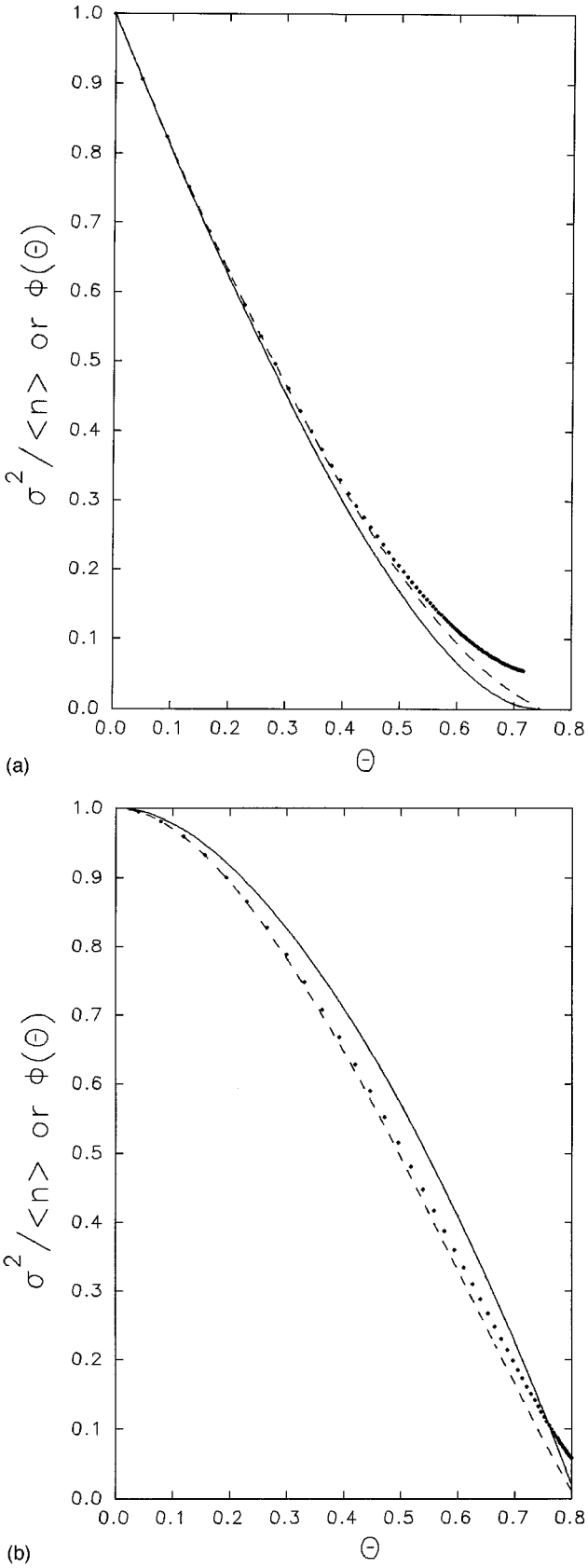
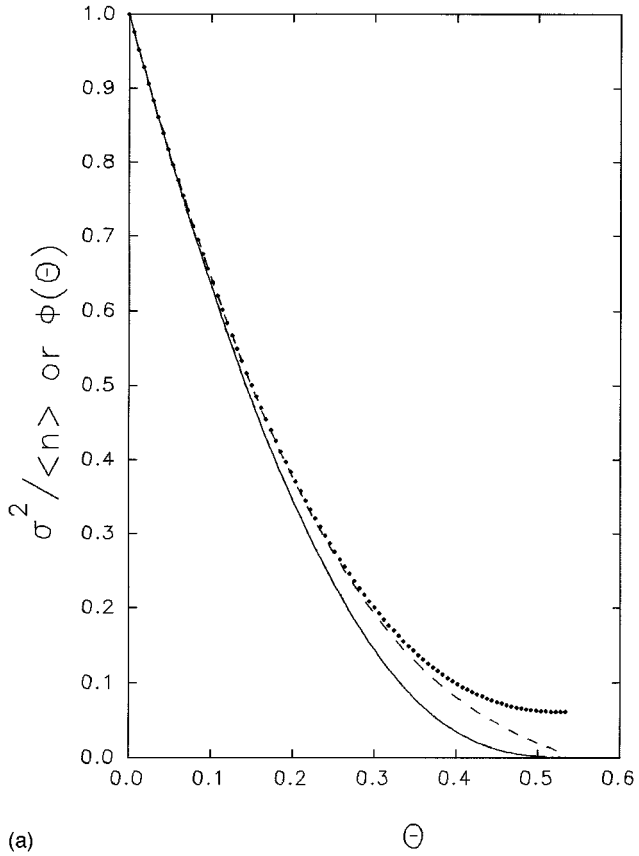
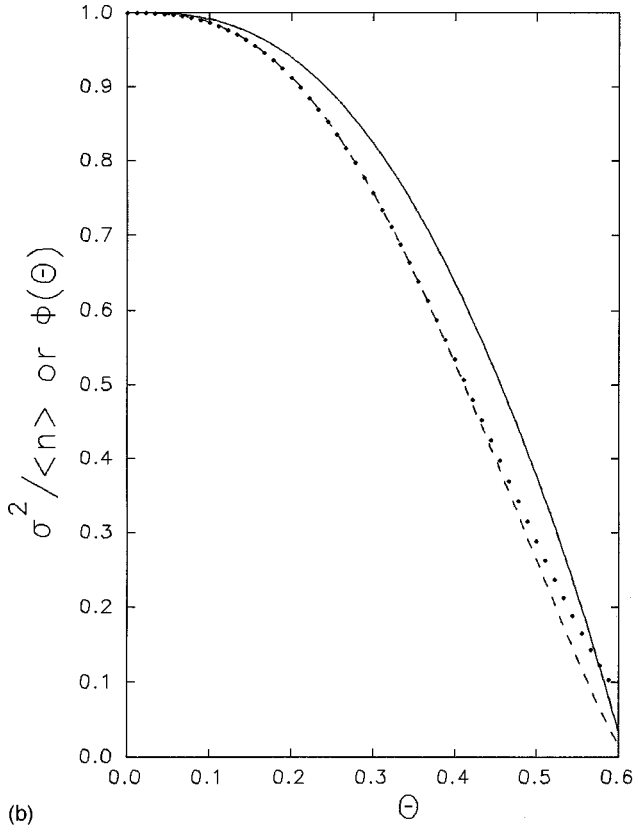


FIG. 1. Exact (• • •) and mean field (---) reduced variances corresponding to the one-dimensional RSA (1a) and BD (1b) models. Exact values of the reduced variance have been obtained using the expression given in Ref. 10. The corresponding available surface functions are also plotted for comparison (—).



(a)



(b)

FIG. 2. Exact (• • •) and mean field (---) reduced variances for two-dimensional models (a: RSA, b: BD), and available surface functions (—). The RSA variance was taken from Ref. 2 and the available surface function from Ref. 14. For the ballistic model, the simulation results have been fitted with 5th-degree polynomials (see text).

cluded by k particles deposited at the positions $\mathbf{r}_1 \ldots \mathbf{r}_k$. The excluded area $A_{\mathrm{ex}}(1\ldots k)$ depends upon the positions of the particles and the interactions between these k particles and the depositing particles from the bulk. Usually it is a positive quantity, but in the case of attraction between particles in the bulk it can become negative. Let $n_2(N,r)$ be the number of pairs of particles deposited on the surface of area A and characterized by a center to center distance ranging from 0 to r given that there are already N particles deposited on the system. This number of pairs is related to the radial distribution function $g(r)$ by the relation:

$$n_2(n,r) = \frac{N}{2}\,\rho \int_0^r 2\pi r' g(r') dr'. \tag{17}$$

For $n_2(N,r)$ to change by the deposition of a new particle, this latter has to deposit within a disk of radius r centered on one of the already N deposited particles. Thus,

$$\frac{dn_2(N,r)}{dN} = \frac{N}{A\Phi(\rho)}\, S_a(r), \tag{18}$$

where $S_a(r)$ represents the probability that a particle arriving over a disk of radius r centered on an already deposited particle will reach the surface, and $A\Phi(\rho)$ corresponds to the probability that a particle arriving over the surface of area A will indeed deposit on it. The probability $S_a(r)$ is related to the k-order generic distribution function through the relation:

$$S_a(r) = \pi r^2 - \frac{\rho^{k-1}}{(k-1)!} \int \ldots \int g^{(k)}(1\ldots k) \times A_{\mathrm{ex}}(1\ldots k) d2\ldots dk + 0(\rho^k), \tag{19}$$

where the integration is performed over a disk of radius r centered on the particle labeled 1. This particle constitutes the ''center particle.'' The term $(k-1)!$ comes from the fact that only k-1 integrations are performed over the positions of the particles labeled $2\ldots k$. The $g^{(k)}(1\ldots k)$ is related to the generic distribution function $\rho^{(k)}(1\ldots k)$ by the relation $\rho^{(k)} \times(1\ldots k) = \rho^k g^{(k)}(1\ldots k)$. By a procedure similar to that developed in Ref. 5, one obtains

$$\frac{1}{A}\frac{dn_2(\rho,r)}{d\rho} = \rho\left\{ \pi r^2 - \frac{\rho^{k-1}}{(k-1)!} \int \ldots \int g^{(k)} \times (1\ldots k) A_{\mathrm{ex}}(1\ldots k) d2\ldots dk \right\} + 0(\rho^{k+1}). \tag{20}$$

Thus, using relations 17 and 4 and integrating over the space, one finds, similarly to Ref. 5, the expression of the reduced variance:

$$\frac{\sigma^2}{\langle n\rangle} = 1 - \frac{2k}{(k+1)}\,\frac{\rho^k}{k!} \int \ldots \int g^{(k)}(1\ldots k) \times A_{\mathrm{ex}}(1\ldots k) d2\ldots dk + 0(\rho^{k+1}). \tag{21}$$

Comparing this result to the expression for $\Phi(\theta)$, one directly obtains relation (13). This analysis shows that relation (13) is

only valid for large subsystems so that boundary effects can be neglected. Otherwise all the particles in a subsystem could not be taken as equivalent and the limiting procedure in which r becomes large would not be allowed. An analysis of this relation for the case of an RSA deposition mechanism, taking boundary effects into account, has been performed in Ref. 2.

It must be emphasized that the treatment presented above is different from that used in Ref. 5 by the fact that the attention has been focused on the change in the number of *pairs* due to the deposition of a new particle, whereas in the previous approach the change in the *mean number of neighbors* at a given distance from already deposited particles has been calculated. The change of the radial distribution function $g(r)$ due to the fact that the new depositing particle also plays the role of a center particle, has thus been omitted in the first analysis presented in Ref. 5.

IV. DISCUSSION AND CONCLUSION

We have established, based on a mean field assumption, the general relation (15) between the reduced variance of the particle number and the available surface function for irreversible sequential deposition processes. We have also shown that this relation gives at least the exact first term of the low coverage expansion (13) of the reduced variance. Comparison with the results corresponding to exact one-dimensional models and simulations of two-dimensional models reveals that the validity of this relation extends from low to intermediate coverages, but that it fails near saturation, where a cancellation of the fluctuations is predicted. This cancellation is a general property of Eq. (15), and it is a direct consequence of the mean field hypothesis: the assumption that the available surface fraction of the finite region S is a function of its coverage only, $\Phi(n/a)$, implies that at jamming the particle number is fixed by the solution of $\Phi(n/a)=0$ whatever the area a of the subsystem. In fact, density fluctuations still exist on the surface, even at jamming.

In order to correct the mean field result, one has to consider that the available surface of the finite region S, Φ_S, is not completely determined by the number n of particles adsorbed on it, but depends also on the microscopic details of the particle distribution. The quantities appearing in the master equation (7) are to be understood as averages over all configurations consisting of n particles adsorbed on S. In these averages, each configuration is weighted with the probability of appearance when the coverage of the large surface R has the value θ. Therefore, in Eq. (7), $\Phi(n/a)$ should be substituted by the corresponding average $\Phi_S(n;\theta)$.

With this change, the master equation (7) and the expressions for the moments (8, 9) continue to be applicable. This yields the exact expression for the variance,

$$\frac{1}{a}\frac{d\sigma^2}{d\theta}=1+\frac{2}{\Phi(\theta)}\langle \delta n\,\delta\Phi_S\rangle_\theta, \tag{22}$$

where $\delta\Phi_S=\Phi_S(n;\theta)-\Phi(\theta)$, and the average refers to all the configurations of the small system S given that the large system R has a coverage θ. This is a general relation between the variance of the number of deposited particles on a small surface and the correlation between the particle number and the available surface fraction.

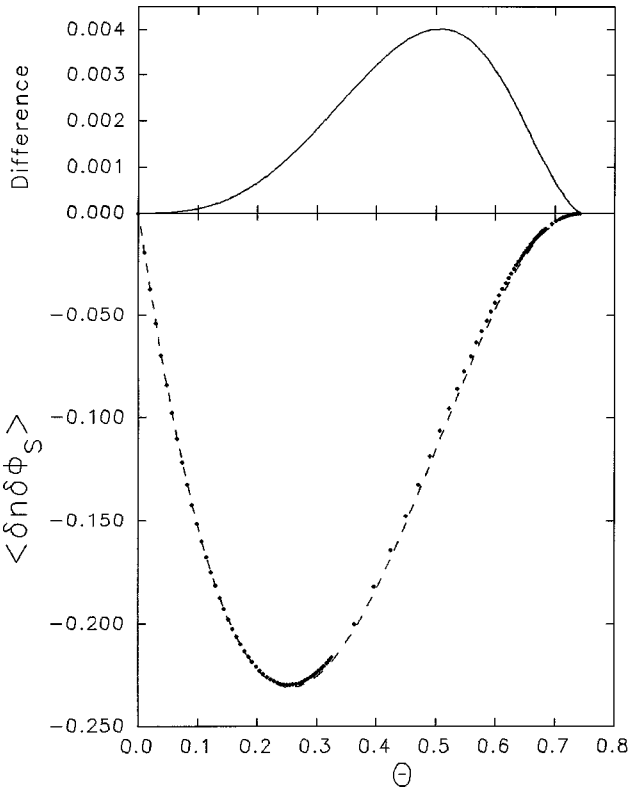


FIG. 3. Exact (• • •) and mean field (---) cross correlation $\langle \delta n\,\delta\Phi_S\rangle$ between the particle number n and the available surface fraction Φ_S, for the one-dimensional RSA model. The exact values have been obtained using Eq. (22) and the exact expression for the reduced variance of the particle number given in Ref. 4. The mean field result has been obtained by numeric integration of Eq. (15), using the exact form of the available line fraction given for example in Ref. 12. The upper part shows the difference (—) between the exact and mean field values.

The mean field theory assumes $\Phi_S(n;\theta)=\Phi(n/a)$, and this leads to $\langle n\rangle/a=\theta$. However, $\Phi(n/a)$ gives the average value of Φ_S for a given value of n, irrespective of θ. The correct average depends also on θ because different configurations with equal number of particles are more likely to appear at different values of θ. We can write

$$\langle \delta n\,\delta\Phi_S\rangle_\theta=\langle \delta n[\Phi(n/a)-\theta(\theta)]\rangle_\theta + \langle \delta n[\Phi_S(n;\theta)-\Phi(n/a)]\rangle_\theta, \tag{23}$$

The first term on the right hand side of Eq. (23) is the only term retained in the mean field approach and the second term, which we will denote $\Delta(\theta)$, gives the correction due to the fluctuations of Φ_S for given n. It is plausible that this latter term will always be positive: for a given value of n, those configurations with larger available surface are expected to appear before and to disappear faster than those with smaller Φ_S; therefore, if $\theta<n/a$ the configurations with large Φ_S are dominant and $\Phi_S(n;\theta)>\Phi(n/a)$, whereas

if $\theta > n/a$ those configurations with smaller Φ_S are more probable and $\Phi_S(n;\theta) < \Phi(n/a)$. In both situations, the contribution to $\Delta(\theta)$ is positive.

As can be seen in Fig. 3 for the one-dimensional RSA, the mean field hypothesis gives a very good approximation to the cross correlation $\langle \delta n \, \delta\Phi_S \rangle$ for all values of the coverage. However, when integrating Eq. (22) to obtain σ^2, these small errors sum up to an appreciable contribution at jamming:

$$\left(\frac{\sigma^2}{\langle n \rangle} \right)_{\text{exact}} = \left(\frac{\sigma^2}{\langle n \rangle} \right)_{\text{mf}} + \frac{2\Phi^2(\theta)}{\theta} \int_0^\theta d\theta' \, \frac{\Delta(\theta')}{\Phi^3(\theta')}. \qquad (24)$$

Equation (24) shows that the mean field assumption underestimates σ^2, and that the nonzero value of the variance at jamming is a consequence of the fluctuations of the available surface on a small subsystem when compared to its mean field value. In general, the description of the fluctuations of Φ_S requires microscopic information about the particle distribution, and Eq. (15) gives all the information about σ^2 that can be obtained from the ''macroscopic'' information contained in $\Phi(\theta)$.

The distribution function approach starts from the exact relation (4). In principle, it can be continued including terms of larger order, which give information about the particle structure relevant for higher coverages. For example, in Ref. 2 the virial expansion of $g(r)$ for the RSA model has been used to obtain the first two terms in the expansion of the reduced variance, whereas in Ref. 10 an exact expression for $g(r)$ has been used to obtain the reduced variance by numerical integration of Eq. (4). However, for the more realistic models it is very difficult to go beyond the first order approach presented here.

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