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To cite this article: P. R. Van Tassel and P. Viot 1997 *EPL* **40** 293

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An exactly solvable continuum model of multilayer irreversible adsorption

P. R. VAN TASSEL(*) and P. VIOT

*Laboratoire Physique Théorique des Liquides, Université Pierre et Marie Curie
4 Place Jussieu, 75252, Paris Cedex 05, France*

(received 28 October 1996; accepted in final form 12 September 1997)

PACS. 68.10Jy – Kinetics (evaporation, adsorption, condensation, catalysis, etc.).

PACS. 82.20Wt – Computational modeling; simulation.

Abstract. – We present a continuum model of irreversible multilayer adsorption where particles are d -dimensional spheres that deposit from the $(d + 1)$ -th dimension onto a d -dimensional substrate. They are considered irreversibly adsorbed if they i) encounter the substrate or ii) land on another previously adsorbed particle. We derive exact expressions, valid in all dimensions, for the density and pair correlation function of the particles in the lowest layer, *i.e.* those contacting the substrate. We find that the first-layer density in irreversible multilayer adsorption is much lower than that found previously in irreversible monolayer adsorption. We further generalize this model to allow depositing particles to adsorb only if they “overhang” empty substrate by an amount less than a certain threshold. We present exact expressions of the density of adsorbed and overhanging particles in one dimension for this general model.

The adsorption of large particles such as colloids and proteins is an important stage of many biological and engineering processes. A quantitative understanding of these systems requires the development of accurate kinetic models [1], [2]. When the rates of diffusion and desorption are small and adsorption occurs only in a single layer, the random sequential adsorption (RSA) model [3] is applicable. In RSA, objects are added sequentially at random positions in d -dimensional space. Any trial leading to overlap with a previously placed object is rejected; this process continues until no further particles may be placed. RSA is exactly solvable in 1D; in higher dimensions, approximate solutions may be obtained [4].

A number of cases have been reported experimentally where adsorption continues beyond one layer, that is, where particles can adsorb onto previously adsorbed particles [5]-[9]. Multilayer adsorption models based on RSA have been formulated to study these systems theoretically. In one dimension, lattice models are available for irreversible multilayer adsorption [10]-[14]. These are typically limited to situations where particles in higher layers can screen unoccupied surface lattice sites only by “bridging” between two lower-layer particles. The effect of “overhanging” a single particle is usually neglected. A hierarchy of rate equations

(*) Present address: Department of Chemical Engineering and Materials Science, Wayne State University 5050 Anthony Wayne Drive, Detroit, MI 48202 USA.

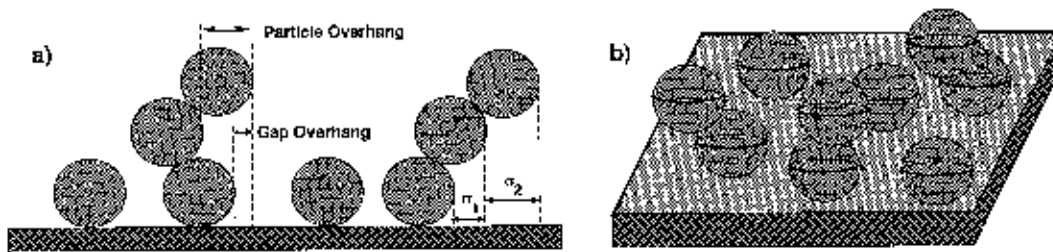


Fig. 1. – A schematic of multilayer deposition of a) disks on a line and b) spheres on a plane. In a), overhangs over empty intervals of the line (gap overhangs) and overhangs over lower-layer particles (particle overhangs) are demonstrated as are examples of overhangs of lengths σ_1 and σ_2 contributing to $\rho_\sigma(t)$.

can be written to describe the kinetics, but unlike the simple RSA model, no exact solution has been obtained, even in one dimension, for layers beyond the first. In two dimensions, numerical simulation of multilayer irreversible adsorption has been performed [15]–[17].

In this letter, we develop a continuum model of multilayer adsorption that i) explicitly allows for screening due to overhangs and ii) is exactly solvable (for the lowest layer) in dimensions greater than 1. Particles are modeled as d -dimensional spheres that deposit onto a d -dimensional substrate from above, *i.e.* from the $(d+1)$ -th dimension. Particles are considered irreversibly adsorbed whenever they reach either the substrate or another particle. Obviously, $d = 2$ corresponds most closely to the physical situation of spheres adsorbing in a multilayer manner onto a flat surface (see fig. 1). The time evolution of the density and pair correlation function of particles in the lowest layer are calculable for all d . This is of particular importance because, in certain cases, the first layer is the most strongly bound and will persist on a surface after rinsing [8]. Additionally, optical techniques can be used to distinguish the first layer from the rest of the deposit as reported by Lavalle *et al.* [9] for a system of adsorbing red blood cells. Finally, mean-field approaches allowing for approximate treatments of upper layers require an accurate solution to the properties of the first layer.

We begin by defining $\Phi_c(\mathbf{r}_1; t)$ as the probability of finding a cavity of radius equal to the particle diameter at vector position \mathbf{r}_1 in the d -dimensional substrate. The time evolution of this function is given by

$$\frac{\partial \Phi_c(\mathbf{r}_1; t)}{\partial t} = -2^d \Phi_c(\mathbf{r}_1; t). \quad (1)$$

(We use reduced units, so the rate of adsorption and the particle diameter are unity.) The solution is simply $\Phi_c(\mathbf{r}_1; t) = \exp[-2^d t]$. The time evolution of the density of particles in the lowest layer is just the probability of placing a particle in such a cavity. Therefore,

$$\frac{d\rho(t)}{dt} = \Phi_c(\mathbf{r}_1; t), \quad (2)$$

and the density is then given by

$$\rho(t) = \frac{1 - e^{-2^d t}}{2^d}. \quad (3)$$

In $2 + 1$ dimensions, the exact saturation density, given simply by 2^{-2} , confirms the value of 0.250 ± 0.001 calculated recently by computer simulation of a system of vertically depositing spheres that adhere upon contact with the surface or another particle [16].

To obtain information on the structure of the particles in the first layer, we next consider the function $\Phi_{cc}(\mathbf{r}_1, \mathbf{r}_2; t)$, the probability of finding cavities whose radii equal the particle diameter at vector positions \mathbf{r}_1 and \mathbf{r}_2 . Its time evolution obeys the following equation:

$$\frac{\partial \Phi_{cc}(\mathbf{r}_1, \mathbf{r}_2; t)}{\partial t} = -V(\mathbf{r}_1, \mathbf{r}_2) \Phi_{cc}(\mathbf{r}_1, \mathbf{r}_2; t), \quad (4)$$

where $V(\mathbf{r}_1, \mathbf{r}_2)$ is the (dimensionless) d -dimensional volume blocked by 2 (perhaps overlapping) particles at positions \mathbf{r}_1 and \mathbf{r}_2 . Since $V(\mathbf{r}_1, \mathbf{r}_2)$ depends only upon the relative distance $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$, $V(\mathbf{r}_1, \mathbf{r}_2) = V(r_{12})$. In 1D, this volume is

$$V(r_{12}) = \begin{cases} 2 + r_{12}, & r_{12} < 2, \\ 4, & r_{12} \geq 2, \end{cases} \quad (5)$$

and in 2 D, the volume is

$$V(r_{12}) = \begin{cases} 8 - \frac{4}{\pi} \left(2 \cos^{-1} \left(\frac{r_{12}}{2} \right) - r_{12} \sqrt{1 - \frac{r_{12}^2}{4}} \right), & r_{12} < 2, \\ 8, & r_{12} \geq 2. \end{cases} \quad (6)$$

It is clear then that $\Phi_{cc}(\mathbf{r}_1, \mathbf{r}_2; t) = \Phi_{cc}(r_{12}; t) = \exp[-V(r_{12})t]$.

Next, consider the function $\Phi_{pc}(\mathbf{r}_1, \mathbf{r}_2; t)$, the density of particles at \mathbf{r}_1 such that a cavity of radius equal to the particle diameter exists at \mathbf{r}_2 . This function evolves according to

$$\frac{\partial \Phi_{pc}(\mathbf{r}_1, \mathbf{r}_2; t)}{\partial t} = -2^d \Phi_{pc}(\mathbf{r}_1, \mathbf{r}_2; t) + \Phi_{cc}(r_{12}; t) \quad (7)$$

and has the following solution:

$$\Phi_{pc}(\mathbf{r}_1, \mathbf{r}_2; t) = \Phi_{pc}(r_{12}; t) = \frac{e^{-2^d t} - e^{-V(r_{12})t}}{V(r_{12}) - 2^d}. \quad (8)$$

This may now be used to calculate the pair correlation function, which evolves according to

$$\frac{\partial}{\partial t} (\rho(t)^2 g(r_{12}; t)) = 2 \Phi_{pc}(r_{12}; t) \quad (9)$$

and is thus given by

$$g(r_{12}; t) = \frac{2}{(V(r_{12}) - 2^d) \rho^2(t)} \left(\rho(t) - \frac{1 - e^{-V(r_{12})t}}{V(r_{12})} \right). \quad (10)$$

It is easy to note that in all dimensions, $g(r_{12}; t) \equiv 1$, when $r_{12} > 2$ for all t . For irreversible monolayer adsorption (simple RSA) in one dimension, the correlations between particles on the surface vanish very rapidly due to a superexponential decay of the correlation function [18]. We note here that in irreversible multilayer adsorption, the correlations cancel beyond a distance larger than the diameter of a particle. This weak correlation is due to the influence of particles in the 2nd and higher layers on those in the 1st layer. Figure 2 compares the pair correlation function from eq. (10) to that of the simple RSA model at the same density. A knowledge of g could have practical use in determining the nature of the deposition as it is known experimentally that the structure of the adsorbed layer is often more sensitive to the deposition characteristics than is the saturation coverage [19].

We now consider the more general case where not all of the particles adhere upon contact with the substrate or with another previously placed particle. We expect that in real systems, particles that significantly extend over an empty surface may be less tightly bound and tend

not to adhere. Restricting ourselves here to one dimension (fig. 1), it is useful to consider the gaps between “clusters” of particles, that is, voids on the line not shadowed by particles in any layer. We assume that any particle i) landing completely within a gap or ii) landing on a previously placed particle but not overhanging a gap more than an amount $\delta (\leq 1)$ will adsorb irreversibly. The kinetics of the filling process for the first layer obeys

$$\frac{d\rho(t)}{dt} = P(x=1, t), \quad (11)$$

where $P(x, t)$ is the probability that a randomly chosen segment of the line of length x is empty at time t . The time evolution of this probability $P(x, t)$ can be written in a closed form for $x \geq 1$,

$$\frac{\partial P(x, t)}{\partial t} = -(x-1)P(x, t) - 2 \int_0^1 du P(x+u, t) - 2 \int_0^\delta dv \int_0^{\delta-v} du P_1(x+u, t), \quad (12)$$

where $P_1(x, t)$ is the density of particles in any layer with an empty interval of at least x on one of its sides. $P(x, t)$ is just the cumulative probability function of $P_1(x, t)$:

$$P(x, t) = \int_x^\infty du P_1(u, t). \quad (13)$$

The first two terms on the right side of eq. (12) account for the destruction of empty intervals of length x due to addition of particles to the 1st layer at the interior and along the edges of empty intervals. They are identical to those of the equation describing the adsorption of particles in the simple RSA model [18]. The last term accounts for the destruction of empty intervals due to addition of particles in the 2nd and higher layers. Assuming a solution of the form

$$P(x, t) = h(t)e^{-(x-1)t}, \quad (14)$$

one can solve for $h(t)$ with the initial condition $h(t=0) = 0$ (corresponding to the line empty of particles at $t=0$) as

$$h(t) = \exp \left[-2\delta t - 2 \int_0^t dt' \frac{e^{-\delta t'} - e^{-t'}}{t'} \right]. \quad (15)$$

Integrating eq. (11) using the results of eqs. (14) and (15) yields

$$\rho(t) = \int_0^t dt' \exp \left[-2\delta t' - 2 \int_0^{t'} dt'' \frac{e^{-\delta t''} - e^{-t''}}{t''} \right]. \quad (16)$$

We note that for the special case of $\delta = 0$, corresponding to no allowable overhangs, eq. (16) reduces to that which was derived previously for irreversible monolayer adsorption (simple RSA) [3]. In this case, no screening of the line by particles in 2nd and higher layers occurs and the 1st-layer formation is controlled only by blocking effects of other particles in that layer. When δ increases, the effect of screening becomes more and more important and the saturation density of the 1st layer decreases (fig. 3). When all overhangs are allowed ($\delta = 1$), eq. (16) reduces to eq. (3) with $\delta = 1$.

In the interest of obtaining an analytical solution to the above model, overhangs are defined with respect to the nearest gap. A second possibility would be to define the overhang with respect to the particle onto which the adsorbing particle lands. Figure 1 clarifies the difference between these two definitions. Although no analytical solution exists for a model based on

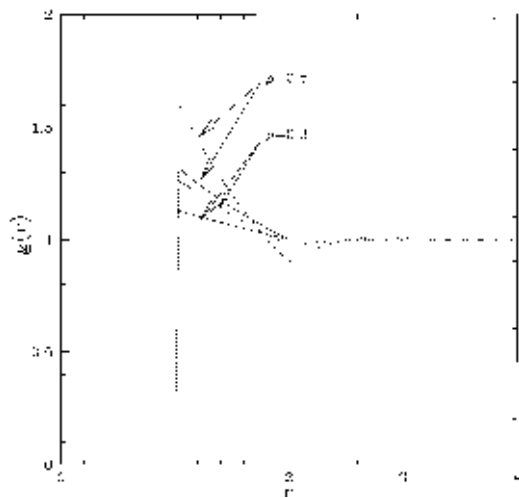


Fig. 2

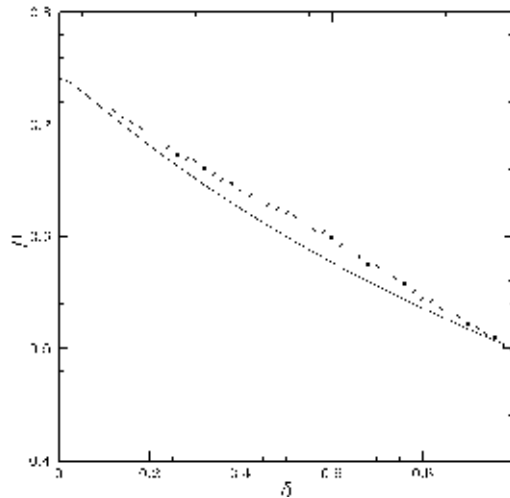


Fig. 3

Fig. 2. – The pair correlation function, $g(r)$, of the 1st layer for $d = 1$ at densities of 0.3 and 0.5. Also shown is the pair correlation function from irreversible monolayer adsorption (the simple RSA model, dotted curves). Note that for the multilayer model, $g(r)$ is equal to unity for $r > 2$ at any density.

Fig. 3. – The saturation densities of the model with gap overhangs (exact results) (full curve) and those of the the model with particle overhangs (simulation results) (crosses) *vs.* the extent of overhang, δ .

particle overhangs, we can obtain numerical data via Monte Carlo simulation. In fig. 3, we compare the saturation densities *vs.* δ for models employing these two different overhang definitions. The saturation density of the model based on gap overhangs is always less than that of the model based on particle overhangs except for the two limits ($\delta = 0$ and $\delta = 1$) where they are equal.

Although a complete solution for the 2nd and higher layers is not available, one can obtain some information on these layers from the probability functions $P(x, t)$ and $P_1(x, t)$. Consider the projection of the overhangs of adsorbed 2nd- and higher-layer particles on the gaps between 1st-layer particles. Let $\rho_\sigma(t)\delta\sigma$ be the density of the particle projections of size between σ and $\sigma + d\sigma$ on the line (see again fig. 1). Noting that the density of the 1st layer is given by the complementary fraction of empty line and the projection of all overhangs, we can write a general sum rule for multilayer adsorption model,

$$\rho(t) = 1 - P(0, t) - \int_0^1 d\sigma \sigma \rho_\sigma(t). \quad (17)$$

This serves to generalize the sum rule for irreversible monolayer adsorption [3].

When $\delta = 1$, at time t , the density $\rho_\sigma(t)$ is governed by

$$\frac{\partial \rho_\sigma(t)}{\partial t} = -2P_1(\sigma, t) + (1 - \sigma)P_2(\sigma, t), \quad (18)$$

where $P_2(x, t)dx$ is the density of pairs of particles separated by an empty interval of length between x and $x + dx$ (also known as the gap distribution function). Solving for $\rho_\sigma(t)$ gives

$$\rho_\sigma(t) = \frac{4 + e^{-(1+\sigma)t}(-4 - 4(1+\sigma)t + (\sigma^3 + \sigma^2 - \sigma - 1)t^2)}{(1 + \sigma)^3}. \quad (19)$$

It is worth noting that the limit of $\rho_\sigma(t)$ when $\sigma \rightarrow 1$ is different than $\rho(t)$ as the former implies contact with a neighboring particle.

As stated in ref. [10], the physics of multilayer deposition is controlled by two steric effects: i) surface blocking by particles in the 1st layer and ii) surface screening by particles in 2nd and higher layers. We present here exact results for the first layer of a d -dimensional, continuum, multilayer adsorption model that accounts for both screening and blocking. This represents a significant extension over previous lattice models that neglect screening and are solvable in only one dimension. In 1D, certain generalizations of this model that allow for a variable extent of screening are also solvable.

Although exact solutions are not available beyond the first layer, mean-field treatments, based on an average surface blockage per particle, can be used to estimate the density and structure of higher layers and to determine the scaling properties of the growing interface [10]-[12]. Our exact, first-layer model appears to offer great promise in further understanding and modeling the full, multilayer process.

PRVT thankfully acknowledges a NATO-NSF Postdoctoral Fellowship. The Laboratoire Physique Théorique des Liquides is Unité de Recherche No. 765 associée au Centre Nationale de la Recherche.

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