

Fractional Deposition of Hard Spherical Particles: Integral-Equation Theory and Monte Carlo Simulation

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Abstract—Deposition of large particles such as colloidal or bio-particles on a solid surface is usually modeled by the random sequential adsorption (RSA). The model was previously described by the integral-equation theory whose validity was proved by Monte Carlo simulation. This research generalized the model to include the concentration effect of added particles on the surface. The fraction of particles inserted was varied by the number density of 0.05, 0.1, and 0.2. It was found that the modified integral-equation theory yielded the results in good accordance with the simulation. When the fraction of particles added was increased, the radial distribution function has higher peak, due to the cooperative and entropic effects. This work could bridge the gap between equilibrium adsorption, where all particles may be considered moving and RSA, where there is no moving particles.

Index Terms—Colloid, Deposition, Integral Equation Theory, Monolayer Films.

I. INTRODUCTION

To understand the onset of irreversibility, it is very useful to generalize the adsorption model by considering the time scales that characterize its various steps. Thus, the generalized adsorption process will depend on at least three distinct characteristic times, assuming that the activation energies for desorption are much higher than for the other processes. Those times are a surface relaxation or diffusion time (τ_d) measuring time for moving one step, a reaction time (τ_r) measuring the time for irreversible attachment to the surface, and an adsorption time (τ_a) measuring the separation between two consecutive adsorption events. The relative magnitude of the three times defined above lead to very different physical situations.

In the equilibrium case there is no reaction with the surface and the adsorbed molecules equilibrate rapidly between successive additions such that $\tau_r \gg \tau_a \gg \tau_d$. In another limiting case, Random Sequential Adsorption (RSA), the adsorbed molecules react with the surface instantaneously but not diffuse, so that $\tau_d \gg \tau_a \gg \tau_r$. In the third limit, Sequential Quenching, the separation in the characteristic

times such that $\tau_a \gg \tau_r \gg \tau_d$. A similar discussion about relative magnitude of the characteristic times was also given by Schaaf and Talbot [1].

Usually, the adsorption of large particles such as colloidal particles and proteins on a surface is irreversible. Feder and Giaever [2] reported that the monolayer structures of adsorbed ferritin on carbon surface could be explained by the model of random sequential adsorption (RSA). Onoda and Liniger [3] also found that the configurations of polystyrene spheres on a glass surface finally reached the jamming limit of RSA. However, there have been many indirect and direct evidences showing that among the immobile particles there exists mobile fraction of particles. Reports of surface coverages significantly greater than the RSA jamming limit provide indirect evidence for lateral diffusion [4]. An early study of surface diffusion of adsorbed proteins was carried out by Michaeli *et al.* in 1980 [5]. In their experiment the distribution of bovine serum albumin (BSA) adsorbed on glass was imaged by autoradiography. They saw no evidence of desorption and noticed that a protein front migrated over distances proportional to the square root of time, as expected for diffusion. Later, Burghardt and Axelrod [6] published a quantitative study of BSA surface diffusion on quartz. They used an elliptical spot fluorescence recovery after photobleaching (FRAP) in a total internal reflection configuration to measure simultaneous surface diffusion and exchange between adsorbed and dissolved proteins in solution. They found that adsorbed BSA exists in three distinct states: irreversible, slowly reversible and rapidly reversible.

Tilton *et al.* [7], [8] used FRAPP based on interference of two coherent beams in total internal reflection at a solid-liquid interface. In their studies, BSA was adsorbed on polymer surfaces: spin-cast polymethyl-methacrylate (PMMA) films and cross-linked spin-cast films of polydimethylsiloxane (PDMS). They found coexistence of a mobile and an immobile population of BSA. Tilton *et al.* [8] also found that the mobile fraction does not depend on surface concentration. The coexistence of mobile and apparently immobile proteins appears to result not from aggregation of adsorbed BSA but from a change in conformation or orientation of the adsorbed protein. Other experiments on protein adsorption, such as that of DNA oligonucleotides on APTES glass [9] and of BSA on silica-titania surfaces [10], have also revealed surface diffusion in the adsorbed state. If the protein-protein interactions are favorable, surface diffusion will lead to clustering [11], [12].

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The model of sequential quenching (SQ) has been studied to describe the effect of surface diffusion in irreversible adsorption on monolayer structures [13], [14]. Nonetheless, only one particles moving at one time is an idealistic situation. In this work, the effect of mobile fraction of hard particles moving among the immobile ones on the surface was investigated in the process called fractional deposition. We varied the number of added particles at each time and they are allowed to diffuse under the effect of other previously adsorbed particles. In Section II, the detail of simulation method is provided and the simulation results together with the discussion are given in Section III. The article is then concluded in Section IV.

II. AN INTEGRAL-EQUATION THEORY FOR FRACTIONAL DEPOSITION

A. Adsorption within Disordered Matrices

A fluid within in a disordered porous matrix can be viewed as a binary mixture of quenched particles (component 0) and equilibrated or annealed particles (component 1), as shown in Figure 1.

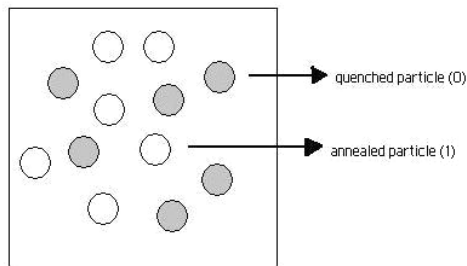


Fig 1: Fluid particles (1) are adsorbed within a quenched matrix (0)

Let $\rho_{00}^{(2)}(r)$ denote pair density function of the quenched structure, let $g_{00}(r) = \rho_{00}^{(2)}(r) / \rho_0^2$ be its pair correlation function and let $h_{00}(r) = g_{00}(r) - 1$ be the residual or total correlation function between two particles separated by a fixed distance r . Similar correlations may be defined for 0-1 and 1-1 pairs. The Replica Ornstein-Zernike equations according to Madden and Glandt [15] and later modified by Given and Stell [16] for such a system are

$$\begin{aligned} h_{00}(r) &= c_{00}(r) + \rho_0 c_{00}(r) \otimes h_{00}(r) \\ h_{01}(r) &= c_{01}(r) + \rho_0 c_{00}(r) \otimes h_{01}(r) + \rho_1 c_{01}(r) \otimes h_{c11}(r) \\ h_{10}(r) &= c_{10}(r) + \rho_0 c_{10}(r) \otimes h_{00}(r) + \rho_1 c_{c11}(r) \otimes h_{10}(r) \\ h_{11}(r) &= c_{11}(r) + \rho_0 c_{10}(r) \otimes h_{01}(r) + \rho_1 c_{c11}(r) \otimes h_{11}(r) \\ &+ \rho_1 c_{b11}(r) \otimes h_{c11}(r) \\ h_{c11}(r) &= c_{c11}(r) + \rho_1 c_{c11}(r) \otimes h_{c11}(r) \end{aligned} \quad (1)$$

where the symbol \otimes denotes a convolution integral. The $c(r)$ in the above equations are the direct correlation functions, i.e. the sums of all coefficients (“diagrams” or

“cluster integrals”) in the density expansions of the corresponding total correlation functions $h(r)$ which are free from nodal points. These cluster integrals are best represented in graphical form; a review of graphical notation can be found in classical references [17]. The sub-indices c and b denote the so-called connected and blocking parts of the 1-1 correlations, distinguishing whether all paths between the roots in their graphical representation pass through a matrix particle or not.

B. Binary-Mixture Approximation

An evolving sequentially or differentially quenched system can be viewed as a binary mixture of the previously quenched particles (denoted by the index 0) and the (infinitely dilute) newly added particles (denoted by 1), of number densities ρ and $d\rho$, respectively as shown in Fig 1. The set of equations in (1) becomes

$$\begin{aligned} h_{00}(r) &= c_{00}(r) + \rho c_{00}(r) \otimes h_{00}(r) \\ h_{01}(r) &= c_{01}(r) + \rho c_{00}(r) \otimes h_{01}(r) + d\rho c_{01}(r) \otimes h_{c11}(r) \\ h_{10}(r) &= c_{10}(r) + \rho c_{10}(r) \otimes h_{00}(r) + d\rho c_{c11}(r) \otimes h_{10}(r) \\ h_{11}(r) &= c_{11}(r) + \rho c_{10}(r) \otimes h_{01}(r) + d\rho c_{c11}(r) \otimes h_{11}(r) \\ &+ d\rho c_{b11}(r) \otimes h_{c11}(r) \\ h_{c11}(r) &= c_{c11}(r) + \rho_1 c_{c11}(r) \otimes h_{c11}(r) \end{aligned} \quad (2)$$

These must be supplemented with an approximate closure such as the Percus-Yevick (PY) relations

$$\begin{aligned} f(r) [1 + h_{01}(r)] &= c_{01}(r) [1 + f(r)] \\ f(r) [1 + h_{11}(r)] &= c_{11}(r) [1 + f(r)] \\ f(r) [1 + h_{c11}(r)] &= c_{c11}(r) [1 + f(r)] \end{aligned} \quad (3)$$

or any alternatives, where $f(r)$ is the Mayer function which is $\exp(-u(r_{12})/kT) - 1$, $u(r)$ is the pair interaction which in this work is hard sphere potential, k is the Boltzmann constant, and T is the temperature. In fractional deposition, when the total density of the system increases from ρ to $\rho + d\rho$, a balance of particle pairs yields the change in the pair density function

$$\begin{aligned} (\rho + d\rho)^2 g_{00}(r; \rho + d\rho) &= \rho^2 g_{00}(r; \rho) \\ &+ 2\rho d\rho g_{01}(r; \rho) + (d\rho)^2 g_{11}(r; \rho) \end{aligned} \quad (4)$$

The first term on the right-hand side represents the pre-existing pairs while the second corresponds to the additional 0-0 pairs created upon quenching of equilibrium particles and the third term is from the contribution of the interaction among added mobile particles. Equation (4) together with its initial condition describes the evolution of a structure built through fractional deposition. As previously

studied, for RSA the third term was negligible since $d\rho$ is comparatively small. The initial condition is

$$g_{00}(r; \rho = 0) = 1 - h_{00}(r; \rho = 0) = \exp(-\beta u(r)) \quad (5)$$

Equation (5) and its PY closure, must be solved for $g_{01}(r)$ and $g_{11}(r)$ at each density in order to compute $g_{00}(r)$ through integration of the differential equation.

C. Numerical Integration

The structure evolves as the density of the system increases, which we denote as ρ_i . On taking the Fourier transform on both sides of (2) and using the fact that total correlation function, $h(r)$, is composed of direct part, $c(r)$, and indirect part, $b(r)$, we obtain algebraic relations,

$$\begin{aligned} \tilde{b}_{c11}(k; \rho_i) &= \frac{\Delta\rho \tilde{h}_{c11}^2(k; \rho_i)}{1 + \Delta\rho \hat{h}_{c11}(k; \rho_i)} \\ \tilde{b}_{01}(k; \rho_i) &= \frac{\rho_i (\tilde{h}_{00}(k; \rho_i) - \tilde{b}_{00}(k; \rho_i)) \tilde{h}_{01}(k; \rho_i)}{1 + \Delta\rho \hat{h}_{c11}(k; \rho_i)} \\ &\quad + \frac{\Delta\rho \tilde{h}_{c11}(k; \rho_i) \tilde{h}_{01}(k; \rho_i)}{1 + \Delta\rho \hat{h}_{c11}(k; \rho_i)} \\ \tilde{b}_{11}(k; \rho_i) &= \frac{\rho_i \tilde{h}_{01}^2(k; \rho_i) - \Delta\rho \tilde{h}_{c11}^2(k; \rho_i) - \rho_i \tilde{h}_{01}(k; \rho_i) \tilde{b}_{01}(k; \rho_i)}{1 + \Delta\rho \hat{h}_{c11}(k; \rho_i)} + \\ &\quad \frac{2\Delta\rho \tilde{h}_{c11}(k; \rho_i) \tilde{h}_{11}(k; \rho_i) + \Delta\rho \tilde{b}_{c11}(k; \rho_i) [\tilde{h}_{c11}(k; \rho_i) - \tilde{h}_{11}(k; \rho_i)]}{1 + \Delta\rho \hat{h}_{c11}(k; \rho_i)} \end{aligned} \quad (6)$$

We use the initial condition to obtain the first $h_{00}(r)$ and $h_{c11}(r)$, and use them together with PY approximations to calculate for $h_{01}(r)$ and subsequently for $h_{11}(r)$. The calculation is repeated using a Picard iteration algorithm at successively larger values of the density, with $\Delta\rho = 0.05, 0.10, \text{ or } 0.20$, i.e. $\rho_{i+1} = \rho_i + \Delta\rho$. Each result for $g_{01}(r)$ and $g_{11}(r)$ is used to compute the next $g_{00}(r)$ from (4), written in discretized form as (7) until the required density is reached.

$$g_{00}(r; \rho_{i+1}) = \frac{\rho_i^2 g_{00}(r; \rho_i) + 2\rho_i \Delta\rho g_{01}(r; \rho_i) + (\Delta\rho)^2 g_{11}(r; \rho_i)}{\rho_{i+1}^2} \quad (7)$$

III. MONTE CARLO SIMULATION

We performed Monte Carlo simulations to verify the accuracy of the numerical results from the Ornstein-Zernike equations. The calculation of the radial distribution function $g(r_i + \Delta r/2)$ is, as customary, based on a histogram for

small increments of width Δr . The averaged distribution function is then trivially obtained as the ratio between number of pairs N_i collected from n configurations, at the separation ranging from r_i and $r_i + \Delta r$ from the average particle to the corresponding number in a system of randomly placed particles.

$$g(r_i + \frac{\Delta r}{2}) = \frac{N_i}{\pi r_i \Delta r \rho N n} \quad (8)$$

where, N_i is the number of particles in the increment $r_i + \Delta r$, N is the total number of particle in the system, and ρ is the number density of the system. To make it dimensionless, the reduced number density is defined as $\rho^* = \rho d^2$.

The details of the simulations are as the following. Particles are added one by one onto a $20d \times 20d$ surface, where d is the hard-core diameter. The number of particles added is 20, 40, or 80 corresponding to $\Delta\rho^* = 0.05, 0.10, \text{ or } 0.20$, respectively. If the added particles overlap with previously quenched particles, they are removed and new additions are attempted until the insertion is successful. This step is followed by classical Metropolis displacement steps, allowing the particles to reach equilibrium under the effect of all other particles. The Markov generates a random walk such that the probability of visiting a particular point \mathbf{r} is proportional to the particle's Boltzmann factor at that location, $\exp(-\beta U(\mathbf{r}))$. Thus, the move from \mathbf{r} to \mathbf{r}' was accepted with probability

$$\text{acc}(o \rightarrow n) = \min(1, \exp\{-\beta[U(\mathbf{r}') - U(\mathbf{r})]\}) \quad (9)$$

Each particle performs a minimum of 1000 accepted moves with a maximum displacement of $0.5d$ before it is quenched in place. The periodic boundary condition is also applied. Our final results, averaged over 100 realizations, are presented in the following section.

IV. RESULTS AND DISCUSSIONS

The results from the integral-equation theory are compared with the ones from simulations. The monolayer was formed by fractional deposition of particles on a homogeneous surface. Each added fraction is equivalent to the number density of 0.1. The examples are shown for the reduced system density, ρ^* , of 0.2, 0.3, and 0.4 in Figures 2, 3, and 4, respectively. As can be seen in Fig.2, at a low system density of 0.2, the simulation gives results in good accord with the theoretical ones. More deviations are observed when the system density increases. This is attributable to the PY approximations, in which some diagrams of higher order of density are neglected. However, the consistency between those is acceptable. This proves the validity of the

integral-equation theory in explaining the evolution of structures built through fractional deposition.

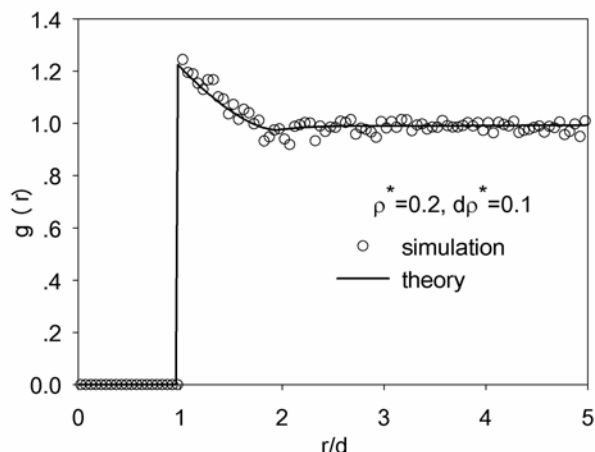


Fig 2: The radial distribution function for the system reduced density of 0.2 generated by depositing a fraction of particles whose added density is 0.1. The theoretical results are compared with the simulation ones.

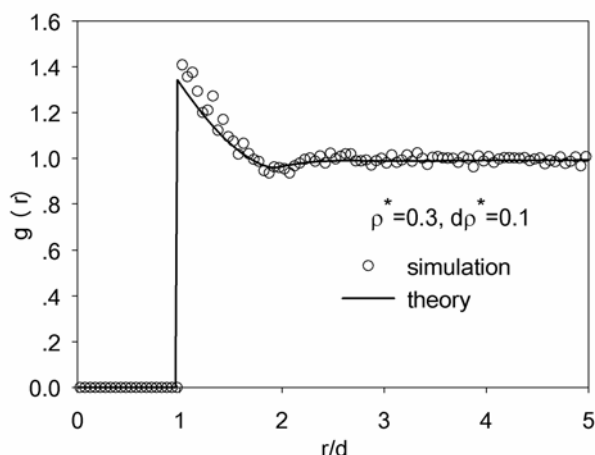


Fig 3: Similar to Fig.2, but the comparison of the results at the reduced number density of 0.3 is made.

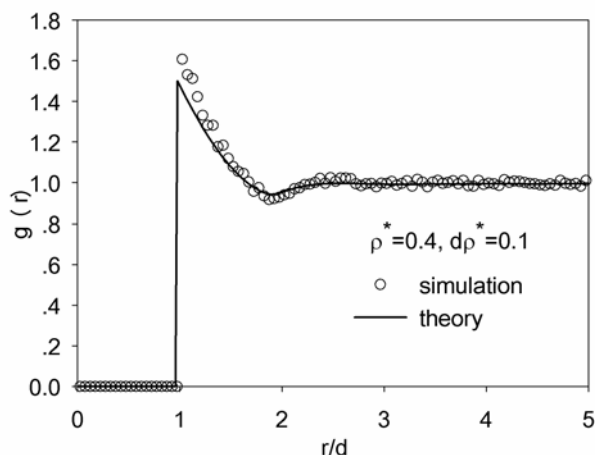


Fig 4: Similar to Fig.2, but the comparison of the results at the reduced number density of 0.4 is made.

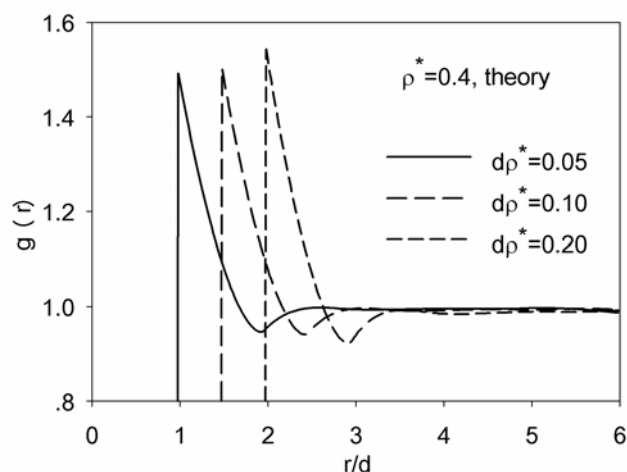


Fig 5: The radial distribution functions from the integral-equation theory, showing the increase of short-ranged order with increasing $d\rho^*$.

Since the interaction between a pair of particles is from a simple hard sphere model, the structure of the radial distribution function shows only the short-ranged interaction, represented by only one prominent peak. This peak is clearly seen higher when the system density increases, resulting from the effect of particle packing on the surface, i.e. in a later addition, the particles will be deposited closer to one another.

The important finding in this study is shown in Fig. 5, where the effect of number of added particles is compared. The system density is kept constant at 0.4, whereas the fraction of particles added is 0.05, 0.10, and 0.20. It is shown that when the fraction of added particles is increased, even though there is no enthalpic effect at all in the system, the entropic effect together with the cooperative effect of all moving particles leads to higher peak of the radial distribution function. Thus, the system of larger $d\rho^*$ is a little more compact and ordered, as was previously found in [18]. The ordered structure contains greater free area for deposition than disordered structures, thereby possessing higher area entropy while losing configurational entropy.

V. CONCLUSION

This work proposed the integral-equation theory based on the Ornstein-Zernike equations to describe the growth of monolayer structures by fractional deposition. The theoretical results are in good agreement with the simulation results. Moreover, the theory is superior to Monte Carlo simulation since the calculation is faster.

Normally, the deposition flux depends on the particle concentration in suspension and the available space on the surface. Therefore, the flux during the monolayer growth should not be assumed constant as has been done in this work. However, the integral-equation theory is amenable to include the variation of $d\rho^*$ along the growing process.

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