구형 생물고분자물질들의 비가역흡착에대한 전달현상의 영향

최호석, Javier Bafaluy* and Julian Talbot**
충남대학 화학공학과, 바르셀로나대학 물리학과*, 퍼듀대학 화학공학과**

Effecrt of transport mechanisms on the irreversible adsorption of spherical biomacromolecules

Ho Suk Choi, Javier Bafaluy* and Julian Talbot**
Department of Chemical Engineering
Chungnam National University, Daejeon City, 305-764, Korea
Departament de Física*
Universitat Autònoma de Barcelona, 08913 Bellaterra (Barcelona), Spain
School of Chemical Engineering**
Purdue University, West Lafayette, IN 47907, USA

Introduction

The adsorption of macromolecules like latexes, proteins, bacteria and enzymes has played an important role in many different industrial fields, which include chromatographic separation, filtration, water cleansing and biofouling. Despite the importance, the theoretical analysis of these processes are still at the beginning stage. The interactions between the adsorbed particles and those in the vicinity of the surface are difficult to account for theoretically. Furthermore, since the adsorption of large molecules and microparticles is often irreversible, one cannot necessarily use the method of equilibrium statistical thermodynamics.

Recently, a realistic model, which specially includes a transport mechanism, has been proposed in which the deposition is represented as a diffusion adsorption of hard spheres[1,2,3]. Through a careful simulation study of 1D diffusion random sequential adsorption (DRSA)[4], the saturation coverage of this process(0.7529) is slightly, but significantly, larger than that of simple 1D RSA(0.747). The reason for this discrepancy is that the diffusion process leads to a non-uniform distribution of particles within the available gaps. In this paper, we extend the generalized parking process to allow for this possibility and compute the saturation coverage which results from an adsorption rate found from both approximate and exact solutions of the steady state diffusion equation.

Non uniform deposition of DRSA

In this section, we describe a general one dimensional model with non-uniform addition rates. We introduce $k(h', h)$ to denote the probability per unit length and per unit time that deposition of a disk in a gap of length $h' > 1$ produces gaps of length h and $h' - h - 1$ (the position of the center of the new disk within the gap is thus $x = h + 1$ relative to the center of the disk on the left of the gap) when the diameter of a particle is 1.

The governing kinetic equation for the adsorption process is:

$$\frac{\partial G(h,t)}{\partial t} = \frac{\partial G(h,t)}{\partial t}\Big|_{loss} + \frac{\partial G(h,t)}{\partial t}\Big|_{creation} \tag{1}$$

$$= -k_0(h)G(h,t) + \int_{h+1}^{\infty} dh' G(h',t)[k(h',t) + k(h',h'-h-1)]$$

where $G(h,t)$ is the number of gaps with length h at time t. If the disks are identical, we expect $k(h',h)$ is a symmetric function, $k(h',h) = k(h',h'-h-1)$. Thus, the above equation can be simplified as follows:

$$\frac{\partial G(h,t)}{\partial t} = -k_0(h)G(h,t) + 2\int_{h+1}^{\infty} dh' G(h',t)k(h',h). \tag{2}$$

This equation together with the initial condition $G(h, t=0) = 0$, and the normalization condition

$$\int_0^{\infty} dh(1+h)G(h,t) = 1 \tag{3}$$

determines completely $G(h,t)$. The function $k_0(h)$ is the total rate at which gaps of length h are destroyed by the addition of a new particle:

$$k_0(h) = \int_0^{h-1} dh' k(h,h') \tag{4}$$

and clearly $k_0(h) = 0$ if $h < 1$.

Let us consider the problem of disks adsorbing irreversibly on a line segment of length h to determine the average number of disks that are in this gap after an infinite time, $N_\infty(h)$. A key observation is that insertion of one disk into the gap at length h produces two additional gaps of length h' and $h-h'-1$. Therefore, one may write the following recursion formula:

$$N_\infty(h) = 1 + 2\int_0^{h-1} N_\infty(h')P(h,h')dh', \tag{5}$$

where $P(h,h')$ is the probability that insertion of a disk into the gap of length h produces gaps of length h' and $h-h'-1$.

Eq.(5) has an interesting by-product. Clearly, we know the initial solutions:

$$N_\infty^{(1)}(h) = 0, \qquad 0 \le h < 1, \tag{6}$$

$$N_\infty^{(2)}(h) = 1, \qquad 1 \le h < 2. \tag{7}$$

Higher order functions may be conveniently and accurately computed numerically using the recurrence relation. The mean saturation coverage of particles adsorbed in a confined gap of size h is

$$\theta_\infty(h) = \frac{N_\infty(h)}{h}. \tag{8}$$

From Rényi's original work[5], one has the following asymptotic relation:

$$\theta_\infty(\infty)-\theta_\infty(h)\sim\frac{1}{h}. \tag{9}$$

To obtain the rate of arrival of Brownian disks at any point of the line, it is necessary to solve the diffusion equation for the probability distribution of the position of the center of the new diffusing particle, $\Psi(r,\theta)$,

$$\nabla^2\Psi=0, \tag{10}$$

where the assumption of quasi-steady state is applied, with an adsorbing boundary along the line,

$$\Psi=0, \qquad at\ z=0, \tag{11}$$

and reflecting boundaries at the exclusion surfaces of the preadsorbed disks:

$$\frac{\partial\Psi}{\partial r}=0, \qquad at\ r=1. \tag{12}$$

Far from the surface, we assume a uniform flux of increasing particles, $\vec{J}=-J_\infty\vec{z}$ in cartesian coordinates and $J_r=J_\infty\cos\theta$, $J_\theta=J_\infty\sin\theta$ in polar coordinates,

$$J^2_\infty=J^2_r+J^2_\theta=constant \qquad as\ r\to\infty. \tag{13}$$

Then, the rate of arrival of new disks at a given point depends on the distribution of previously adsorbed disks on the entire line. Nevertheless, it is natural to assume that only the nearest disks, i.e., those located at the ends of the free gap, have a noticeable influence.

If only one disk has been adsorbed, the steady solution of the diffusion equation is, using polar coordinates centered at the center of the fixed disk,

$$\Psi(r,\theta)=(r+1/r)\cos\theta, \qquad r>1 \tag{14}$$

from which one obtains the rate of arrival of new disks at a point at distance r from the center, $J(r)|_{z=0}=-D(\partial\Psi/\partial z)_{z=0}=J_\infty(1+1/r^2)$. The flux of disks increases in the vicinity of the origin ($r>1$) as a consequence of reflecting from the fixed disk. Now, in the absence of disks, $J=J_\infty$. If two disks are present, we assume as a first approximation that the deviations from this value produced by each disk are independent and can be added. Thus, $J(r)\approx1+1/r_1^2+1/r_2^2$, r_1 and r_2 being the distance to the centers of each disk. After normalization one finds

$$P_1(h',h)=\frac{h'}{(h'-1)(h'+2)}[1+(h+1)^{-2}+(h'-h)^{-2}]. \tag{15}$$

Then, a first approximation to the DRSA process is obtained using P_1 as valid for any value of h' and h in the recursion relation (5). From the extrapolation of $\theta_\infty(h)$ vs $1/h$ curve to $1/h=0$, we obtain $\theta_\infty=0.750621\pm0.000022$ confirming that both methods give the same coverage values.

In order to assess the accuracy of the independent disk assumption used alone, we have also obtained the exact solution of the deposition problem in the presence of 2 disks. In bipolar coordinate system- ξ, η, the diffusion equation now reads

$$\frac{\partial^2 \Psi}{\partial \eta^2} + \frac{\partial^2 \Psi}{\partial \xi^2} = 0. \tag{16}$$

with boundary conditions

$$\Psi = 0, \qquad at\ \xi = 0,\ \pi, \tag{17}$$

$$\frac{\partial \Psi}{\partial \eta} = 0, \qquad at\ \eta = \pm\alpha. \tag{18}$$

Therefore, the problem is separable. The normalized result for the particle flux in the region between the disks is given by the convergent series

$$J = \frac{1}{2c}[1 + 2(1 + \cosh\eta) \sum_{n=1}^{\infty} \frac{(-1)^{n+1} n e^{-n\alpha}}{\sinh n\alpha} \cosh\eta]. \tag{19}$$

This J is exactly the function P_2. It depends on $h' = L-1$ through the coefficients α and c and on h through the coordinate η of the arriving point ($x = c\tanh\eta/2$ and $h = L/2 - x - 1$). After inserting (19) into (5) and computing numerically, one finds a value of the coverage $\theta_\infty \approx$ 0.75102, only slightly different from the result obtained with P_1. $\theta_\infty \approx$ 0.7506. Thus, even a first approximation can be enough to estimate the jamming coverage of DRSA process.

Conclusion

We have developed a general kinetic equation for 1D non-uniform deposition processes and recursion formulae for the saturation coverage. In DRSA, the non-uniformity is induced by the diffusion of the adsorbing molecules. The saturation coverage obtained from the first approximation does not differ greatly from that correspond to the exact analytic solution in the process of two disks. These results are also consistent with numerical simulations of the DRSA process, if proper allowance (throughout a scaling relation) is taken of the finite lattice of the simulation. Moreover, the position dependent flux of the particles obtained from the simple approximate solution of the diffusion equation is consistent with the data obtained from Monte Carlo simulation of DRSA.

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