



BRIDGING FLOCCULATION : A MODELING STUDY OF THE ROLE OF POLYMER ADSORPTION DYNAMICS

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ABSTRACT

Polymer adsorption from solution to solid surface plays an important role in bridging flocculation. It is desirable to understand the dynamics of adsorption for a number of reasons. For example, the balance between flocculation and stabilization of a colloidal suspension can be affected by the dynamics of adsorption. Although a number of experimental studies on kinetics of polymer adsorption have been reported in the literature, there is a need for a comprehensive model for diffusion in the interfacial region.

Such a model is proposed in this paper. The connectivity of the homopolymer segments is assumed to be described by a random flight model within the framework of mean field theory while the dynamics of the probability of the connected segment is given by the Smoluchowski equation. The model yields the profiles for evolution of surface excess with time. This is then compared with surface excess obtained from equilibrium calculations. It is found that the surface excess predicted by the dynamical model at long times is the same as that predicted by equilibrium calculations. The dynamical adsorption behavior of homopolymers of different chain lengths is also studied. It is found, as expected, that longer chains adsorb more than the smaller chains and tend to equilibrate slower than smaller chains.

Key words: Polymer adsorption, Mean field theory, Bridging flocculation.

INTRODUCTION

Polymer adsorption from solution to solid surface plays an important role in a variety of industrial applications including flocculation, stabilization of colloidal suspensions, biocompatibility, adhesion, lubrication, anti-redeposition and soil release in detergent formulation¹. It is desirable to understand the dynamics of adsorption for a number

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of reasons. For example, the balance between flocculation and stabilization of a colloidal suspension can be affected by the dynamics of adsorption². A slowly adsorbing polymer may favor flocculation by attaching to a large number of colloidal particles, while a rapidly adsorbing polymer may bring about stabilization by adsorbing as a dense layer on individual particles. Although a number of experimental studies on kinetics of polymer adsorption have been reported in the literature, there is a need for a comprehensive model for diffusion in the interfacial region. The objective of the present work is to formulate such a model within the framework of mean field theory.

EXPERIMENTAL

Model development

Consider an infinitely large volume of agitated solution consisting of monodisperse, straight chain and uncharged homopolymer and a monomeric solvent species. The polymeric species is assumed to be made of r correlation segments, each having length ℓ . The solution is assumed to be dilute with respect to the polymeric species. It is assumed that at time $t \leq 0$ the concentrations are uniform throughout the solution. At time $t = 0$, a plane, adsorbing surface of infinite length and width is introduced into the solution. The surface is situated at $z = 0$ with the z -axis normal to the surface (Fig. 1).

The kinetics of polymer adsorption can be described as a four phenomena process (note that these phenomena are not necessarily sequential but can occur simultaneously):

1. Diffusion controlled regime with negligible interaction between chains.
2. Formation of a complete monolayer with a distribution of loops, trains and tails.
3. Further adsorption of chains requires penetration of the layer and conformational rearrangement of the adsorbed chains.
4. Desorption of chains.

We consider steps 1 and 2 alone in this work. Step 3 has been considered in using reptation dynamics.³ As for step 4, we consider the special case that the adsorption-desorption dynamics takes place much faster than the diffusion dynamics.

The concentrations of species are expressed in terms of volume fractions. Thus the following equality holds at any location in the system:

$$\phi_p(z, t) + \phi_s(z, t) = 1 \quad \dots(1)$$

where ϕ_p and ϕ_s refer to the volume fractions of polymer and solvent, respectively. We divide the solution into two subregions. The region between $z = 0$ and $z = \delta$ is the region where the concentration of the polymer is in the semidilute/concentrated regime. Here the mean-field approximation is valid. The region between $z = \delta$ and $z \rightarrow \infty$ is the bulk region where the concentration of a species is independent of z . The bulk concentrations are denoted by superscript b. Thus,

$$\phi_p^b + \phi_s^b = 1 \quad \dots(2)$$

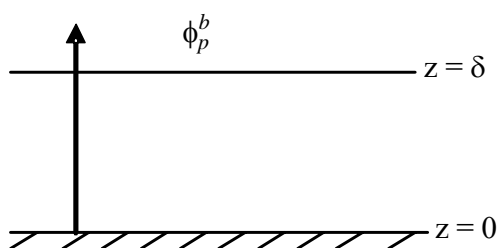


Fig. 1: Schematic of the interfacial region. The region between $z = 0$ and $z = \delta$ is the adsorbed layer region

It is assumed that the bulk concentration of the polymer does not vary with time. This assumption is reasonable when the quantity of the polymer adsorbed is small compared to that present in the solution at $t = 0$.

Using an elementary material balance, it can be shown that –

$$v_p J_p(z, t) + v_s J_s(z, t) = 0 \quad \dots(3)$$

where J_p and J_s are the diffusive fluxes for the polymer segment and the solvent molecule, respectively. v_p and v_s are the volumes of the polymer segment and solvent molecule, respectively. The diffusive fluxes can be written in the form of the following equations –

$$J_p(z, q, t) = -D_{ps} \left[\frac{\phi_p(z, q, t)}{v_p} \right] \frac{\partial}{\partial z} \left[\frac{u_p(z, q, t)}{k_B T} + \ln \phi_p(z, q, t) \right] \quad \dots(4)$$

$$J_s(z,t) = -D_{ps} \left(\frac{\phi_s(z,t)}{v_s} \right) \frac{\partial}{\partial z} \left[\frac{u_s(z,t)}{k_B T} + \ln \phi_s(z,t) \right] \quad \dots(5)$$

Here D_{ps} is the binary diffusion coefficient for polymer segment-solvent. It is dependent on the composition of the solution and hence it is a function of z . It is, however, expected to be independent of the contour coordinate of the segment. The terms, $u_p(z,q,t)$ and $u_s(z,t)$ represent the mean-field potentials acting on the segment and solvent, respectively.

Equation (4) can be integrated with respect to q to yield.

$$J_p(z,t) = -\frac{D_{ps}}{v_p} \left[\frac{1}{k_B T \ell} \int_0^{\ell} \phi_p(z,q,t) \frac{\partial u_p(z,q,t)}{\partial z} dq + \frac{\partial \phi_p(z,t)}{\partial z} \right] \quad \dots(6)$$

Multiplying (6) by v_p and v_s adding them and making use of (1) and (3), we obtain

$$\frac{1}{\ell} \int_0^{\ell} \phi_p(z,q,t) \frac{\partial u_p(z,q,t)}{\partial z} dq + (1 - \phi_p(z,t)) \frac{\partial u_s(z,t)}{\partial z} = 0 \quad \dots(7)$$

Equation (7) relates the potential acting on a polymer segment with that on the solvent molecule.

Consider the region, encompassing the adsorbed layer (i.e. the region between $z = 0$ and $z = \delta$), the governing equations are:

$$\frac{1}{v_p} \frac{\partial \phi_p(z,q,t)}{\partial t} = -\frac{\partial J_p(z,q,t)}{\partial z} \quad \dots(8)$$

where
$$J_p(z,q,t) = -D_{ps} \left[\frac{\phi_p(z,q,t)}{v_p} \right] \frac{\partial}{\partial z} \left[\frac{u_p(z,q,t)}{k_B T} + \ln \phi_p(z,q,t) \right] \quad \dots(9)$$

Combining (8) and (9), we obtain the Smoluchowski equation in the following form –

$$\frac{\partial \phi_p(z,q,t)}{\partial t} = D_{ps} \frac{\partial}{\partial z} \left[\frac{\phi_p(z,q,t)}{k_B T} \frac{\partial u_p(z,q,t)}{\partial z} + \frac{\partial \phi_p(z,q,t)}{\partial z} \right] \quad \dots(10)$$

The initial and the boundary conditions associated with the above equation are:

$$\phi_p(z, q, 0) = \frac{\phi_p^b}{r} \quad \dots(11)$$

$$\phi_p(\delta, q, t) = \frac{\phi_p(\delta, t)}{r} \quad \dots(12)$$

The boundary condition at $z = 0$ is a composite boundary condition and is obtained as follows –

$$\frac{\partial \phi_p^*(q, t)}{\partial t} = -a_p J_p(0, q, t) \quad \dots(13)$$

$$\text{where } J_p(0, q, t) = -D_{ps} \left[\frac{\phi_p(0, q, t)}{v_p} \right] \frac{\partial}{\partial z} \left[\frac{u_p(0, q, t)}{k_B T} + \ln \phi_p(0, q, t) \right] \quad \dots(14)$$

Combining (13) and (14), we obtain –

$$\frac{\partial \phi_p^*(q, t)}{\partial t} = D_{ps} \left(\frac{a_p}{v_p} \right) \left[\frac{\phi_p(0, q, t)}{k_B T} \frac{\partial u_p(0, q, t)}{\partial z} + \frac{\partial \phi_p(0, q, t)}{\partial z} \right] \quad \dots(15)$$

We assume that at any instant the surface phase is in equilibrium with the solution at $z = 0$. This allows us to write the following relation between $\phi_p^*(q, t)$ and $\phi_p(z, q, 0)$.

$$\frac{\phi_p^*(q, t)}{\phi_p(0, q, t)} = \exp \left(\frac{u_p^*(q, t) - u_p(0, q, t)}{k_B T} \right) \quad \dots(16)$$

Equation (15), in conjunction with (16) constitutes the boundary condition at $z = 0$ for (10).

The potential acting on a polymer segment, $u_p(z, q, t)$ consists of two parts.

$$u_p(z, q, t) = u_p^l(z, t) + u_p^{nl}(z, q, t) \quad \dots(17)$$

The local part $u_p^l(z, t)$ arises out of the interactions of the segment with the local surrounding. It depends on z and t but not on the location of the segment in the chain. The non-local part $u_p^{nl}(z, q, t)$ arises due to the connectivity of the segment with the chain. It

reflects the potential gradient in the interfacial region. If there were no potential gradient in the interfacial region, $u_p^{nl}(z, q, t)$ would be zero. When the potential gradient exists, different segments, located at different z experience different local potentials. They transmit this potential to the other segments through connectivity. Thus a segment in a chain experiences a net pull arising out of all the segments transmitting their pulls on it. The non-local potential, therefore depends on z , t and q . For a monomeric species, such as solvent species, the local potential is the sole contributor to the total potential. We can write the local potential of the polymer segment as –

$$u_p^l(z, t) = \frac{V_p}{V_s} \left[u^0(z, t) - \chi k_B T (\phi_p(z, t) - \phi_p(\delta, t)) \right] \quad \dots(18)$$

Note that the reference state chosen here is the solution at $z = \delta$. The potential $u^0(z, t)$ is the excluded volume potential. It should be chosen in such a way that (1) is satisfied. This needs the simultaneous solution of the Smoluchowski equation for the solvent. We avoid this by make use of (7) to obtain $u^0(z, t)$.

$$\frac{1}{\ell} \int_0^{\ell} \phi_p(z, q, t) \frac{\partial u_p(z, q, t)}{\partial z} dq + (1 - \phi_p(z, t)) \frac{\partial u_s(z, t)}{\partial z} = 0 \quad \dots(19)$$

The boundary condition for the above equation is $u_p(\delta, q, t) = 0$ and $u_s(\delta, t) = 0$. Note that this equation is obtained by combining the Smoluchowski equations for both the segment and the solvent and hence contains all the information needed to obtain $u^0(z, t)$. Here $u_s(z, t)$ is given by the following equation.

$$u_s(z, t) = u^0(z, t) + \chi k_B T (\phi_p(z, t) - \phi_p(\delta, t)) \quad \dots(20)$$

Combining (19) and (20), we obtain -

$$\frac{1}{\ell} \int_0^{\ell} \phi_p(z, q, t) \frac{\partial u_p(z, q, t)}{\partial z} dq + (1 - \phi_p(z, t)) \left(\frac{\partial u^0(z, t)}{\partial z} + \chi k_B T \frac{\partial \phi(z, t)}{\partial z} \right) = 0 \quad \dots(21)$$

Since $u_p(z, q, t)$ itself involves $u^0(z, t)$, (21) needs to be solved iteratively.

There is no direct way of computing $u_p(z, q, t)$. We however use an indirect technique. Suppose at instant t , we freeze the composition of the interfacial region and allow a polymer chain to equilibrate with this solution. Then, $g_p(z, q, t)$, the probability of finding the

(connected) segment of this chain with contour coordinate q at location z , is obtained from the Boltzmann distribution as –

$$g_p(z, q, t) = \exp\left(-\frac{u_p(z, q, t)}{k_B T}\right) \quad \dots(22)$$

Note that since the segment is connected, $u_p(z, q, t)$, in (22), contains both the local and the non-local contributions. Inverting (22), we obtain

$$u_p(z, q, t) = -k_B T \ln g_p(z, q, t) \quad \dots(23)$$

Thus, if we can compute $g_p(z, q, t)$ corresponding to the instantaneous composition of the interfacial region, we can obtain $u_p(z, q, t)$ through (23). We obtain $g_p(z, q, t)$ as follows. We first solve the connectivity equation for the fictitious chain in equilibrium with the instantaneous field. This is written as follows –

$$\ell \frac{\partial G_p(z, q, t)}{\partial q} = \frac{\ell^2}{6} \frac{\partial^2 G_p(z, q, t)}{\partial z^2} + \left[1 - \exp\left(-\frac{u_p^1(z, t)}{k_B T}\right)\right] G_p(z, q, t) \quad \dots(24)$$

Here $G_p(z, q, t)$ is the probability of finding the end segment of a subchain of contour length q at location z at time t . Note that potential used in this equation is the local contribution and is independent of q . It is computed from (19), in conjunction with (22). The polymer volume fractions used in these equations is the instantaneous values.

The initial and the boundary conditions used for solving (24) are⁴:

$$G_p(z, 0, t) = \exp\left(-\frac{u_p^1(z, t)}{k_B T}\right) \quad \dots(25)$$

$$G_p(\delta, q, t) = 1 \quad \dots(26)$$

$$\ell \frac{\partial G_p(0, q)}{\partial q} = \left[1 + 2 \exp\left(-\frac{u_p^{*1}(t) - u_p^1(0, t)}{k_B T}\right)\right]^{-1}.$$

$$\left(\frac{\ell}{2} \frac{\partial G_p(0, q, t)}{\partial z} + G_p(0, q, t) \left\{ 1 - 2 \exp\left(\frac{u_p^1(0, t)}{k_B T} \right) + 2 \exp\left(-\frac{u_p^{*1}(t) - u_p^1(0, t)}{k_B T} \right) \right\} \right) \quad \dots(27)$$

The potential $u_p^{*1}(t)$ is given by the following equation –

$$u_p^{*1}(t) = \frac{v_p}{v_s} \left[u^{*0}(t) - \chi \cdot k_B T (\varphi_p(t) - \phi_p(\delta, t)) + \chi_p^* k_B T \right] \quad \dots(28)$$

For the solvent, we have –

$$u_s^*(t) = u^{*0}(t) + \chi \cdot k_B T (\varphi_p^*(t) - \phi_p(\delta, t)) + \chi_s^* k_B T \quad \dots(29)$$

From (16), we have –

$$\frac{\varphi_p^*(q, t)}{\phi_p(0, q, t)} = \exp\left(\frac{u_p^*(q, t) - u_p(0, q, t)}{k_B T} \right) \quad \dots(30)$$

Since the non-local potential of a segment in the surface phase is expected to be that same as that at $z = 0$, we can rewrite the above equation as –

$$\frac{\varphi_p^*(q, t)}{\phi_p(0, q, t)} = \frac{\varphi_p^*(t)}{\phi_p(0, t)} = \exp\left(\frac{u_p^{*1}(t) - u_p^1(0, t)}{k_B T} \right) \quad \dots(31)$$

or
$$u_p^{*1}(t) - u_p^1(0, t) = k_B T \ln\left(\frac{\varphi_p^*(t)}{\phi_p(0, t)} \right) = k_B T \ln\left(\frac{\varphi_p^*(q, t)}{\phi_p(0, q, t)} \right) \quad \dots(32)$$

This is the relation, which is to be used in Eq. (27).

Now
$$u_p^{*1}(t) - u_p^1(0, t) = \frac{v_p}{v_s} \left[u^{*0}(t) - u^0(0, t) - \chi \cdot k_B T (\varphi_p(t) - \phi_p(\delta, t)) \right] + \chi k_B T (\varphi_p(0, t) - \phi_p(\delta, t)) + \chi_p^* k_B T \quad \dots(33)$$

Combining Eq. (32) and (33), we obtain

$$k_B T \ln\left(\frac{\varphi_p^*(t)}{\phi_p(0, t)} \right) = \frac{v_p}{v_s} \left[u^{*0}(t) - u^0(0, t) - \chi \cdot k_B T (\varphi_p(t) - \phi_p(\delta, t)) \right] + \chi k_B T (\varphi_p(0, t) - \phi_p(\delta, t)) + \chi_p^* k_B T \quad \dots(34)$$

Similarly for solvent species –

$$\frac{\phi_s^*(t)}{\phi_s(0,t)} = \exp\left(\frac{u_s^*(q,t) - u_s(0,t)}{k_B T}\right) \quad \dots(35)$$

or

$$u_s^*(t) - u_s(0,t) = k_B T \ln\left(\frac{1 - \phi_p^*(t)}{1 - \phi_p(0,t)}\right) \quad \dots(36)$$

and

$$u_s^*(t) - u_s(0,t) = \begin{bmatrix} u^{*0}(t) - u^0(0,t) + \chi' k_B T (\phi_p(t) - \phi_p(\delta,t)) \\ -\chi k_B T (\phi_p(0,t) - \phi_p(\delta,t)) + \chi_s^* k_B T \end{bmatrix} \quad \dots(37)$$

Combining Eq. (36) and (37), we obtain –

$$k_B T \ln\left(\frac{1 - \phi_p^*(t)}{1 - \phi_p(0,t)}\right) = \begin{bmatrix} u^{*0}(t) - u^0(0,t) + \chi' k_B T (\phi_p(t) - \phi_p(\delta,t)) \\ -\chi k_B T (\phi_p(0,t) - \phi_p(\delta,t)) + \chi_s^* k_B T \end{bmatrix} \quad \dots(38)$$

We multiply (38) by (v_p/v_s) and subtract (34) from it to get –

$$\left(\frac{v_p}{v_s}\right) \ln\left(\frac{1 - \phi_p^*(t)}{1 - \phi_p(0,t)}\right) - \ln\left(\frac{\phi_p^*(t)}{\phi_p(0,t)}\right) = \left(\frac{v_p}{v_s}\right) \begin{bmatrix} 2\chi' (\phi_p^*(t) - \phi_p(\delta,t)) \\ -2\chi (\phi_p(0,t) - \phi_p(\delta,t)) + \chi_s^* - \chi_p^* \end{bmatrix} \quad \dots(39)$$

We define

$$\chi^* = \left(\frac{v_p}{v_s}\right) (\chi_s^* - \chi_p^*) \quad \dots(40)$$

Hence Eq. (38) can be rewritten as –

$$\left(\frac{v_p}{v_s}\right) \ln\left(\frac{1 - \phi_p^*(t)}{1 - \phi_p(0,t)}\right) - \ln\left(\frac{\phi_p^*(t)}{\phi_p(0,t)}\right) = \left(\frac{v_p}{v_s}\right) \begin{bmatrix} 2\chi' (\phi_p^*(t) - \phi_p(\delta,t)) \\ -2\chi (\phi_p(0,t) - \phi_p(\delta,t)) \end{bmatrix} + \chi^* \quad \dots(41)$$

Equation (41) provides a relation between ϕ_p^* and $\phi_p(0,t)$

The probability $g_p(z,q,t)$ is obtained as –

$$g_p(z, q, t) = G_p(z, q, t) G_p(z, r\ell - q, t) \exp\left(\frac{u_p^1(z, t)}{k_B T}\right) \quad \dots(42)$$

It is more illuminating to express $g_p(z, q, t)$ as the ratio –

$$g_p(z, q, t) = \frac{r\phi_p^e(z, q, t)}{\phi_p(\delta, t)} \quad \dots(43)$$

where $\phi_p^e(z, q, t)$ represents the volume fraction of polymer segment, in equilibrium with the instantaneous field $u_p^1(z, t)$. We can rewrite Eq. (10) as –

$$\frac{\partial\phi_p(z, q, t)}{\partial t} = D_{ps} \frac{\partial}{\partial z} \left[\phi_p(z, q, t) \frac{\partial \ln(\phi_p(z, q, t)/\phi_p^e(z, q, t))}{\partial z} \right] \quad \dots(44)$$

Once the volume fraction profiles are obtained, the surface excess can be calculated using the equation:

$$\Gamma^{\text{ex}}(t) = \int_0^{\infty} (\phi_p(z, t) - \phi_p^b) dz \quad \dots(45)$$

Model simulation and results

The model described in the previous section is first nondimensionalized. Then it is made amenable to simulations. We choose a finite element method to discretize the equations along z . This results in a set of ODEs in time, which have to be solved in conjunction with a set of nonlinear algebraic equations.

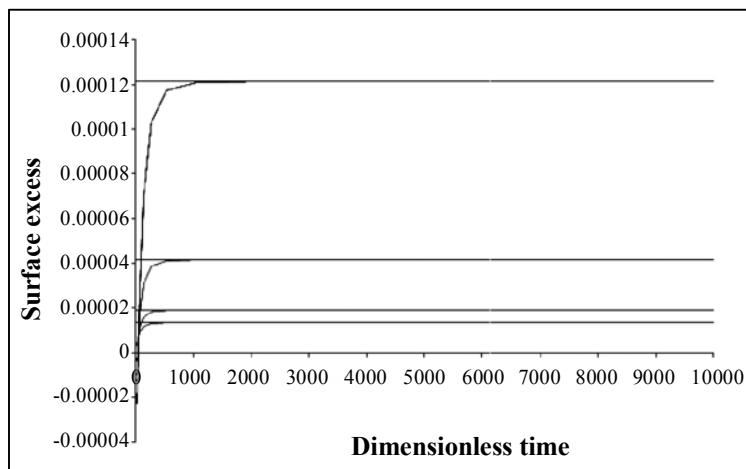


Fig. 2: Surface excess profiles for $r = 1$ (bottom-most curve), $r = 2$, $r = 5$ and $r = 10$ (top-most curve)

In the set of ODEs the equilibrium profiles $\phi_p^e(\hat{z}_j, \hat{q}_s, \hat{t})$ (where the hat denotes dimensionless variables) are to be supplied. This is done using the equilibrium equations⁴, which are solved for using the subroutine CONLES. The set of DAEs are then solved using DSPAK subroutine which is a DAE solver. The DSPAK package is chosen because we are dealing with a linearly implicit system of first order ODEs involving sparse Jacobian matrices and nonlinear algebraic equations.

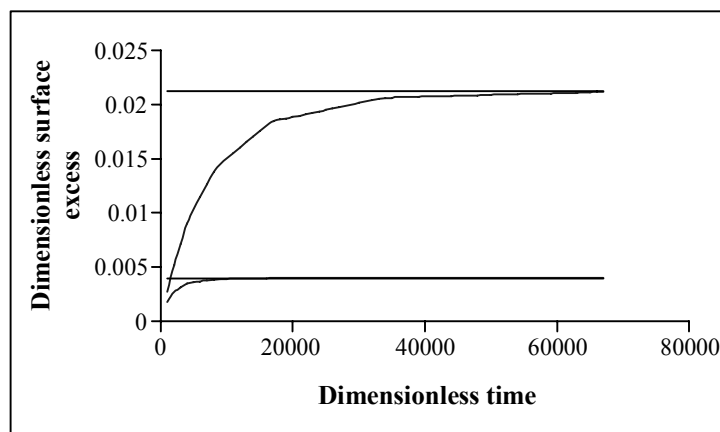


Fig. 3: Surface excess profiles for $r = 30$ (bottom) and $r = 40$ (top)

The model simulations were carried out for the following parameter values:

$$\ell = 1; \delta = 100; \phi_p^b = 10^{-5}; \chi = 0.4; \chi^* = 0.0; \theta = 100.$$

The evolution of surface excess with time are plotted in Figures 2 and 3 for the following cases: $r = 1$, $r = 2$, $r = 5$, $r = 10$, $r = 30$ and $r = 40$. It can be seen that in each case the surface excess tends towards equilibrium, which is indicated by the horizontal lines. The slope is steeper at initial times but then levels out as time proceeds. It is also seen that as chain length increases, the system reaches equilibrium more slowly.

Thus, the model is seen to capture the qualitative features of the adsorption process while quantitative agreement needs to be studied.

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