Adsorption Dynamics. Extension of Self-Consistent Field Theory to Dynamical Problems

Ryuichi Hasegawa*,†,‡ **and Masao Doi**‡

Yokkaichi Research Center, Mitsubishi Chemical Company, Toho-cho, Yokkaichi,
Mie 510, Japan, and Department of Applied Physics, Nagoya University, Chikusa-ku,
Nagoya, Aichi 464, Japan

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ABSTRACT: We propose a new simulation scheme to describe polymer dynamics at interfaces. Using this scheme, we studied adsorption dynamics in a polymer solution. We calculated the evolution of the density profiles and the polymer conformation. The numerical results are qualitatively consistent with recent experimental observations.

Introduction

The process whereby polymers in solution adsorb on a bare surface typically involves adsorption−desorption dynamics and has attracted considerable attention both theoretically and experimentally.[1−6] It is known that the process involves a large structural charge of the adsorbed layer: the conformation of the adsorbed polymers change from a random-coil to a stretched structure as the adsorption proceeds. Previous theories dealt with the dynamics in the limiting cases before and after the adsorbed layer was formed but did not examine the structural change itself. In this paper, we study this problem using a new simulation scheme. The method is a dynamical version of the mean field theory which was first proposed by Fraaije[7] for the microphase separation kinetics of block copolymers. The scheme calculates the free energy density at each time step in solving the diffusion equation. For the present problem, the results provide detailed information on the evolution of the structure of the adsorbed layer including the segment density and the fractions of trains and loops, etc.

Formulation

We consider a bare surface with no adsorbed polymer which is inserted into a polymer solution at time $t = 0$ and ask how the density profile of polymer segments changes in time as the polymers adsorb on the surface. We assume the z coordinate is perpendicular to the surface with its origin located at the surface. Let $\Phi_p(z,t)$ and $\Phi_s(z,t)$ be the dimensionless densities of polymer segment and solvent molecules respectively at time t and position z. The polymer segment density $\Phi_p(z,t)$ consists of two parts, $\Phi_a(z,t)$, the segment density of adsorbed polymers which have at least one segment adsorbed on the surface, and $\Phi_f(z,t)$, the segment density of free polymers which have no adsorbed segments:

$$\Phi_p(z,t) = \Phi_a(z,t) + \Phi_f(z,t) \tag{1}$$

The time evolution of $\Phi_a(z,t)$ and $\Phi_f(z,t)$ is determined by the diffusion of polymer segments driven by the gradient of the chemical potential and the adsorption−desorption dynamics taking place at the surface. Accounting for these two processes in the general case is a complex problem. In this paper, we consider the special case that the adsorption−desorption dynamics takes place much faster than the diffusion dynamics. In such a case, the exchange between the adsorbed polymer and the free polymer takes place very frequently, and they are in equilibrium. Therefore in determining the time evolution of the segment density, we need not distinguish segments of the adsorbed polymer and those of the free polymer: we can first determine the time evolution of the total segment density $\Phi_p(z,t)$, and then calculate $\Phi_a(z,t)$ and $\Phi_f(z,t)$ from the condition that they are in equilibrium for a given total segment density profile $\Phi_p(z,t)$.

We assume that $\Phi_p(z,t)$ and $\Phi_s(z,t)$ satisfies the incompressibility condition.

$$\Phi_p(z,t) + \Phi_s(z,t) = 1 \tag{2}$$

Therefore, the concentration profile is described by a single field $\Phi(z,t)$.

$$\Phi(z,t) = \Phi_p(z,t) - \Phi_s(z,t) \tag{3}$$

Let $F[\Phi]$ be the free energy of the whole system for a given density profile $\Phi(z)$. The diffusion of polymer segments (and solvent molecules) is driven by the gradient of the chemical potential $\delta F/\delta\Phi$. Thus we may assume that the time evolution of $\Phi(z,t)$ is determined by the following diffusion equation

$$\frac{\partial \Phi}{\partial t} = \nabla M \nabla \frac{\partial F}{\delta \Phi} \tag{4}$$

where M is the mobility coefficient, which is in general a function of the local segment density. For the sake of simplicity, we use a "free draining" picture in this paper and assume that M is constant.

The free energy functional $F[\Phi]$ is written as

$$\begin{aligned} F[\Phi] &= F_0[\Phi] + \int_0^\infty \chi \Phi_p \Phi_s \, dz - \chi_s \Phi_p(0) \\ &= F_0[\Phi] + \int_0^\infty \frac{\chi}{4}(1 + \Phi)(1 - \Phi) \, dz - \\ &\qquad \frac{\chi_s}{2}(1 + \Phi(0)) \end{aligned} \tag{5}$$

where χ (and χ_s) are dimensionless parameters, representing the interaction between polymer segments and solvent molecules (and between polymer segments and the surface), and $F_0[\Phi]$ is the conformational entropy

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* To whom correspondence should be addressed. *Phone: 81-593-45-7096. FAX: 81-593-45-7044.*

† Mitsubishi Chemical Co.

‡ Nagoya University.

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part of the free energy: $F_0[\Phi]$ is the free energy of an athermal system in which χ and χ_s are equal to zero.

To calculate $F_0[\Phi]$, we consider an athermal system which has a density profile $\Phi(z,t)$ which is in equilibrium subject to a hypothetical external potential field $V(z,t)$. If the external potential field $V(z,t)$ is known, the functional derivative $\delta F_0/\delta\Phi$ is given by

$$\frac{\delta F_0}{\delta\Phi} = -V \tag{6}$$

Thus from eqs 5 and 6, $\delta F/\delta\Phi$ is calculated as

$$\frac{\delta F}{\delta\Phi} = -V - \frac{\chi}{2}\Phi - \frac{\chi_s}{2}\delta_{z0} \tag{7}$$

To obtain an expression for the potential field $V(z,t)$, we assume that the polymer segments and the solvent molecules are in equilibrium under hypothetical external potential field $V_p(z,t)$ and $V_s(z,t)$ each acting on the polymer segments and the solvent molecules respectively.

$$V(z,t) = V_p(z,t) - V_s(z,t) \tag{8}$$

We now find the potentials $V_p(z,t)$ and $V_s(z,t)$ which give the density profiles $\Phi_p(z,t)$ and $\Phi_s(z,t)$ for an equilibrium athermal system.

It is easy to obtain $V_s(z,t)$. Under an external potential $V_s(z,t)$, the equilibrium density profile of the solvent is given by

$$\Phi_s(z,t) = (1 - \Phi^b)\exp(-V_s(z,t)) \tag{9}$$

where Φ^b is the bulk concentration of the polymer $\Phi^b = \lim_{z\to\infty}\Phi_p(z,t)$. Thus the potential field $V_s(z,t)$ is given by

$$V_s(z,t) = -\ln\left(\frac{\Phi_s(z,t)}{(1-\Phi^b)}\right) \tag{10}$$

To obtain $V_p(z,t)$ we use the self-consistent field theory for polymer statistics. The polymer segment density $\Phi_p(z,t)$ satisfies the following equation

$$\Phi_p(z,t) = \frac{\Phi^b}{N}\int_0^N \Psi_p(z,n,t)\Psi_p(z,N-n,t)\,\mathrm{d}n \tag{11}$$

where $\Psi_p(z,n,t)$ is the solution of the following Schrödinger-type equation

$$\frac{\partial\Psi_p}{\partial n} = \frac{a^2}{6}\nabla^2\Psi_p - V_p\Psi_p \tag{12}$$

where a is the segment size with the "initial" condition and the boundary condition respectively

$$\Psi_p(z,0,t) = 1 \tag{13}$$

$$\Psi_p(z,n,t) = 0 \quad z < 0 \tag{14}$$

From the above set of equations eqs 11–14, the potential field $V_p(z,t)$ can be calculated using the discrete version of the self-consistent field theory as described in ref 9.

Equations 4–7 determine the time evolution of $\Phi(z,t)$. The initial condition is that the segment density is uniform at time $t = 0$, i.e., $\Phi_p(z,0) = \Phi^b$ or $\Phi(z,0) = 2\Phi^b - 1$. The boundary condition is that there is no flux at the wall, i.e. $\partial(\delta F/\delta\Phi)/\partial z = 0$ at $z = 0$. The unit of length is taken to be the segment size a, and the unit of time, the segmental diffusion time a^2/M, which approximately corresponds to the time it takes for a segment to diffuse a distance a by cooperative diffusion.

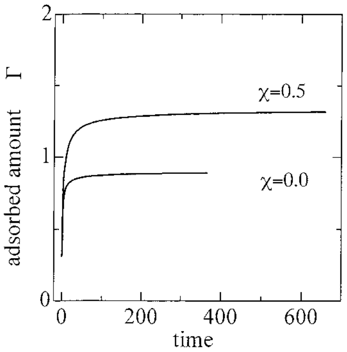

Figure 1. Time development of the amount of adsorbed polymer when a bare surface is inserted into a polymer solution of concentration of Φ^b, where the chain length $N = 30$, polymer–solvent interaction parameter $\chi = 0, 0.5$, and polymer–surface interaction parameter $\chi_s = 1.0$.

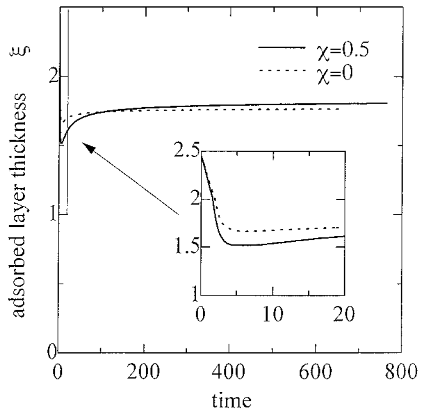

Figure 2. Time evolution of the thickness of adsorbed layer, $\xi(t)$. The solid line represents the case of $\chi = 0.5$ and the dashed line represents the case of $\chi = 0.0$.

Solution of the time evolution equation gives $\Phi(z,t)$, $\Phi_p(z,t)$, and $V_p(z,t)$. If these quantities are known, the details of the conformational statistics can be easily calculated. For example, the density profile $\Phi_f(z,t)$ of the free polymer is calculated from the following set of equations:

$$\Phi_f(z,t) = \frac{\Phi^b}{N}\int_0^N \Psi_f(z,n)\Psi_f(z,N-n)\,\mathrm{d}n \tag{15}$$

$$\frac{\partial\Psi_f}{\partial n} - \frac{a^2}{6}\nabla^2\Psi_f - V_p\Psi_f \tag{16}$$

$$\Psi_f(z,0) = 1 - \delta_{z0} \tag{17}$$

$$\Psi_f(0,n) = 0 \tag{18}$$

The density profile $\Phi_a(z,t)$ of the adsorbed polymer is calculated using

$$\Phi_a(z,t) = \Phi_p(z,t) - \Phi_f(z,t) \tag{19}$$

Similarly, other statistical details, such as the average length and numbers of trains, loops, and tails etc, can be calculated using the method of Scheutjen and Fleer.[10]

Results and Discussion

As illustration of the theory, we present results for $\chi = 0$ (good solvent), and $\chi = 0.5$ (Θ solvent). The values

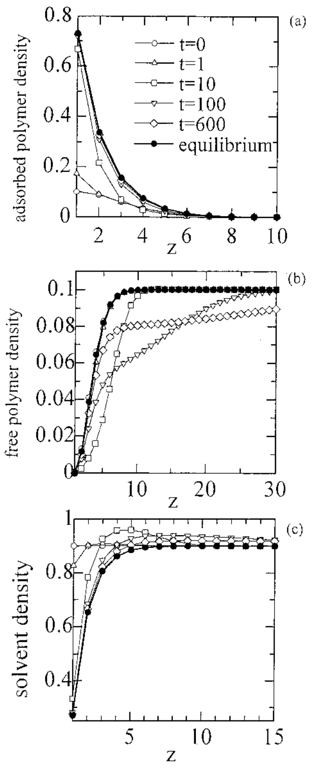

Figure 3. Time evolution of the density profile during adsorption. From top to bottom, are shown the density profiles of (a) the segments of adsorbed polymer, (b) the segments of free polymer, and (c) solvent molecules. The constants are $\chi = 0.5$, $N = 30$, $\Phi^b = 0.1$, and $\chi_s = 1.0$.

of the other constants are $N = 30$, $\Phi^b = 0.1$ and $\chi_s = 1.0$.

Figure 1 shows the time evolution of the adsorbed amount

$$\Gamma = \int_0^\infty \Phi_a(z)\, dz \tag{20}$$

Initially, adsorption takes place very rapidly, but then it slows down considerably. This behavior is similar to that obtained experimentally.[5,6] Clearly, the equilibrium value of the adsorbed amount is larger in a poor solvent than in a good solvent.

Figure 2 shows the time evolution of the thickness of the adsorbed layer

$$\xi(t) = \frac{\int_0^\infty z\Phi_a(z,t)\, dz}{\int_0^\infty \Phi_a(z,t)\, dz} \tag{21}$$

It is seen that $\xi(t)$ first decreases and then increases again: The reason for this behavior will be discussed below.

Figure 3 shows the time evolution of the density profiles of each component, $\Phi_a(z,t)$ (the adsorbed polymer), $\Phi_f(z,t)$ (the free polymer), and $\Phi_s(z,t)$ (the solvent molecules). The equilibrium density profile in Figure 3 is calculated using the usual static self-consistent field theory. It is seen that the profile of the adsorbed layer approaches the equilibrium shape quickly, but the density profile of the free polymer varies very slowly in time. Also notice that in the intermediate stage ($t \simeq 10$), there appears a peak in the solvent density at the edge of the adsorbed layers $z \simeq 4$. The peak in the solvent density corresponds to the depletion of the polymer segment at the edge of the adsorbed layer.

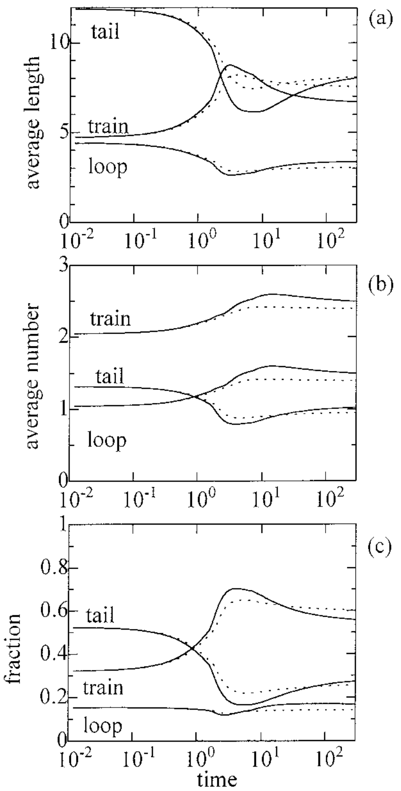

Figure 4. Time evolution of the average quantities of tails, trains, and loops. From top to bottom are shown (a) the average length, (b) the average number per chain, and (c) the fraction of segments belonging to tails, trains, and loops. The solid line represents the case of $\chi = 0.5$, and the dashed line represents the case of $\chi = 0.0$.

Figure 4 shows some structural changes which take place in the adsorbed polymer. Following ref 11, we call a consecutive sequence of adsorbed segments a train, the part between the successive trains, a loop, and the part between a train and the end of the polymer, a tail. Figure 4a shows the time evolution of the average length (the number of segments) of trains, loops, and tails of the adsorbed polymers. Notice that the length of the trains has a maximum at $t \simeq 10$, while the length of the tails and loops has minimum at about the same time. Similar behavior is observed in the fraction of trains, tails and loops (Figure 4c).

The behavior shown in Figures 2–4 suggests the following picture of the adsorption dynamics. The adsorption process consists of two stages. In the first stage ($0 < t \lesssim 10$), the polymers which happen to have segments near the surface are adsorbed on the bare surface. If this happens, the other segments connected to those segments are also adsorbed on the surface. This results in an increase in the average length of the trains and a decrease in the length of tails and loops. During this process, the adsorbed polymers become more flattened, and the thickness of the adsorbed layer decreases. Consequently, there appears a polymer depletion layer near the surface which corresponds to the peak in the solvent density in Figure 3c.

In the second stage of adsorption ($t \gtrsim 10$), the free polymers penetrate into the adsorbed layer. The second stage is very slow compared with the first stage, since the free polymers have to diffuse into the adsorbed layer and reach the surface. As this happens, some adsorbed segments in the existing layer are replaced by the segments of free polymer. Accordingly, the average length of trains decreases, and the average lengths of tails and loops increase.

The picture described here is qualitatively consistent with the recent experimental observation by Granick et al.[12] They observed that as adsorption proceeds, the number of segments which are oriented perpendicularly to the wall first decreases and then increases again. If we assume that segments in trains are parallel to the wall and segments in loops and tails are (in the first approximation) perpendicular to the wall, their results are consistent with our results in Figure 4c.

The present formulation is useful for other problems such as the replacement dynamics[5,6] or the chemical reaction between polymers[13] where the dynamics is coupled with the conformational changes of the polymers. Such problems are now being studied, and the results will be published in the future.

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