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Kinetics of Polymer–Surface Adsorption Using Virial Coefficients

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ABSTRACT: The rate equation for the adsorption of a polymer to a surface depends on the density of sites that can accommodate a variety of polymer conformations. Assuming equilibration on the surface, the density of appropriate sites can be calculated from the virial coefficients obtained from equilibrium statistical mechanics. The first two derivatives of the density as a function of time are given exactly by this process. The construction of the time evolution for the adsorption process is illustrated explicitly, using the virial coefficients obtained in the previous paper.[1]

1. Introduction

In the present paper we consider the kinetics of binding of polymer molecules from solution onto a regular surface, here modeled as the plane-square lattice. The process is illustrated in Figure 1a. We will assume for simplicity that the natural polymer conformations are commensurate with the structure of the lattice. Thus we use the plane-square lattice to model both the allowed polymer conformations (as treated in the previous paper[1] hereafter referred to as paper 1) and the surface. This correspondence need not be the case, but this assumption greatly simplifies the presentation of the basic ideas. The present work builds on previous work on lattice gas models for the kinetics of adsorption and the use of statistical mechanics to treat kinetics.[2-4] In the present work we are making the simplifying assumption that a molecule in the solution phase will adsorb only if there are enough contiguous sites on the lattice surface to accommodate the entire polymer molecule in any one of its conformations. A more complicated version of the model would be to allow partial adsorption of the molecules and subsequent rearrangement on the surface. In order to treat that case we would need mixture virial coefficients that gave information about the number of partial sites available. One could treat that model using the present approach; it involves, however, a much more complicated set of equilibrium virial coefficients. In order to illustrate the approach we thus treat the case where the binding to the surface is very strong and hence only structures with the entire molecule adsorbed need be considered.

In Figure 1a we have placed a marker (solid circle) on one end of the polymer. This is simply an artifact to keep track of the density: the net density of polymers on the lattice is the fraction of sites containing the marker. If one has a lattice of M sites and a polymer of n units the net density has the allowed range

$$0 < \rho < 1/n \tag{1.1}$$

Figure 1b illustrates the essential feature of the adsorption process, namely, that an adsorption site must be able to contain the n contiguous units of the polymer in one of its allowed conformations. The only cooperative effect that we will deal with here is excluded volume; thus a site is defined by the number and type of available lattice positions. The closed boxes in Figure 1b illustrate several potential binding sites; we note that the sites can overlap. We note further that the irreducible set of binding sites is the same as the irreducible set of polymer conformations as shown in Figures 2 and 3 of paper 1 for various n. The members of the irreducible set and the appropriate ω rotations are shown here in Figure 2 for $n = 2$ and 3. We take S_i as the probability of the ith species in the irreducible set of binding sites.

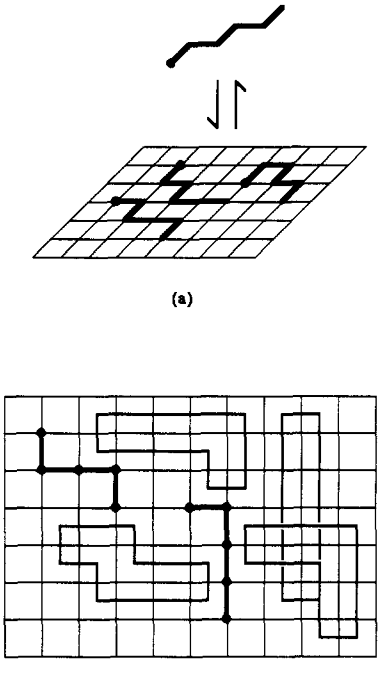

Figure 1. (a) Schematic representation of a polymer molecule adsorbing onto a surface. (b) View of the lattice surface showing polymers adsorbed and potential binding sites (closed boxes).

The kinetic equation for the adsorption of a polymer in conformation i is then simply

$$d\rho_i^*/dt = k_f z_p S_i - k_b \rho_i^* \tag{1.2}$$

where ρ_i^* is the probability that a lattice site contains the end marker (see Figure 1a) of species i in a particular orientation, z_p is the activity of polymers in solution, and k_f and k_b are the forward and backward rate constants, respectively, for the adsorption process. In paper 1 we used ρ_i to represent the probability of species i regardless of orientation; i.e., $\rho_i = \omega_i \rho_i^*$. The net density of polymer bound is simply

$$\rho = \sum_{i=1}^{\sigma} \rho_i = \sum_{i=1}^{\sigma} \omega_i \rho_i^* \tag{1.3}$$

where σ is the number of conformations in the irreducible set, as discussed in paper 1. In writing (1.2) we assume that the polymer remains on the lattice in its initial conformation until it desorbs; that is, we do not allow

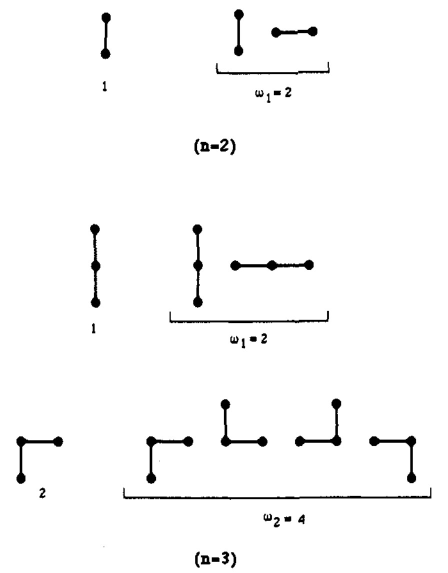

Figure 2. Irreducible set of conformations and the appropriate ω rotations for $n = 2$ and 3.

surface diffusion or conformational transitions on the surface.

The kinetics for the net density is then given by

$$d\rho/dt = k_f z_p S - k_b \rho \tag{1.4}$$

where the net number of binding sites (sum over all conformations and rotations and reflections thereof) is

$$S = \sum_{i=1}^{\sigma} \omega_i S_i \tag{1.5}$$

To treat the activity of the polymer in solution in more detail we require the following initial concentrations:

C_p = original concentration of polymer in solution

C_s = original concentration of potential binding sites (1.6)

The two concentrations must be expressed in the same units (e.g., moles/liter). If there are M lattice sites, the original number of potential binding sites is M/n; If this number is converted to the moles of such sites, the original concentration of binding sites is then given by dividing the moles of sites by the total volume of the solution in contact with the surface. If we treat the polymer solution as ideal (we do not need to make this assumption, but to circumvent it would require a theory for a nonideal polymer solution) one has

$$c = C_s/C_p \tag{1.7}$$

Using (1.7) in (1.4), the net kinetic equation becomes

$$d\rho/dt = k_f C_p (1 - c\rho) S - k_b \rho \tag{1.8}$$

The problem is, of course, that in order to integrate this equation one must known $S(\rho)$, i.e., the number of available binding sites of the proper shape as a function of the number of molecules bound to the surface. This in general is a very difficult quantity to calculate. We illustrate the problem in the following section by constructing the differential equations for the S_i.

2. Rate Equations for Binding Sites

We use the case of $n = 2$ (dimers) to illustrate the general procedure for writing down the rate equations for the various binding sites, S_i. In this case there is only one type of binding site (illustrated in Figure 3a), which has two orientations ($\omega_i = 2$). The processes that decrease the probability of the binding site, that is, the binding of a dimer such that at least one of the sites in S_1 is covered (and hence S_1 is no longer a binding site), are shown in Figure 3b. If i is the index for the type of binding site (indexing a member of the irreducible set of sites) and j is the index for the conformation of the polymer destroying the site (by overlapping with it), then we denote by $S_{ij}^{(k)}$ a particular class of structures with $\omega_{ij}^{(k)}$ being the number of such structures with similar geometries (interconvertible by rotation or reflection)

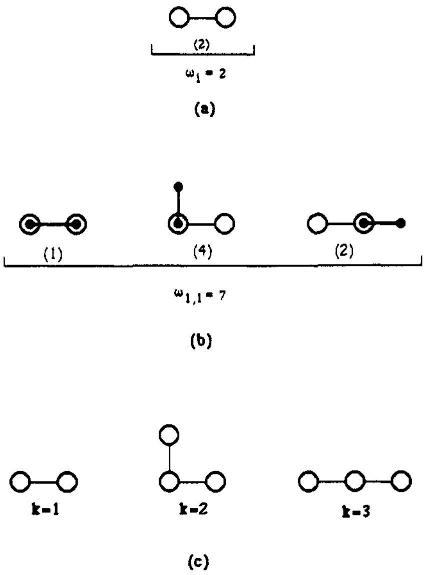

Figure 3. Illustration of binding sites involved in the adsorption kinetics of dimers. (a) The basic site, S_1, required for the adsorption of a dimer. (b) The adsorption configurations whereby the adsorption of a dimer destroys the binding site in (a). (c) The three types of lattice configurations required to construct the differential equation for the rate of change of the probability of the basic binding site in (a).

$\omega_{ij}^{(k)}$ = number of structures of type k derived from a site of type i overlapped by a polymer of conformation j

$$\omega_{ij} = \sum_k \omega_{ij}^{(k)} \tag{2.1}$$

The numbers $\omega_{ij}^{(k)}$ are given in parentheses in Figure 3b; the sum of these, for the dimer model, gives $\omega_{1,1} = 7$, as indicated in Figure 3b. Figure 3c shown the three types of structure $S_{ij}^{(k)}$.

The differential equation for the dimer case is then ($\rho_1^* = \rho/2$)

$$dS_1/dt = -k_f z_p \sum_{k=1}^{3} \omega_{1,1}^{(k)} S_{1,1}^{(k)} + k_b \rho_1^* \tag{2.2}$$

The $k_b\rho_1^*$ term represents the effect of the dimer leaving the surface and hence opening up a new site S_1.

Figures 4 and 5 illustrate the processes whereby the binding sites for the case $n = 3$ are destroyed by being partially (or wholly) covered by a bound polymer. For the case of $n = 3$ there are only two species in the irreducible set (see Figure 2) and yet one sees that there are a very large number of structures that must be considered in order to construct the differential equations for S_1 and S_2.

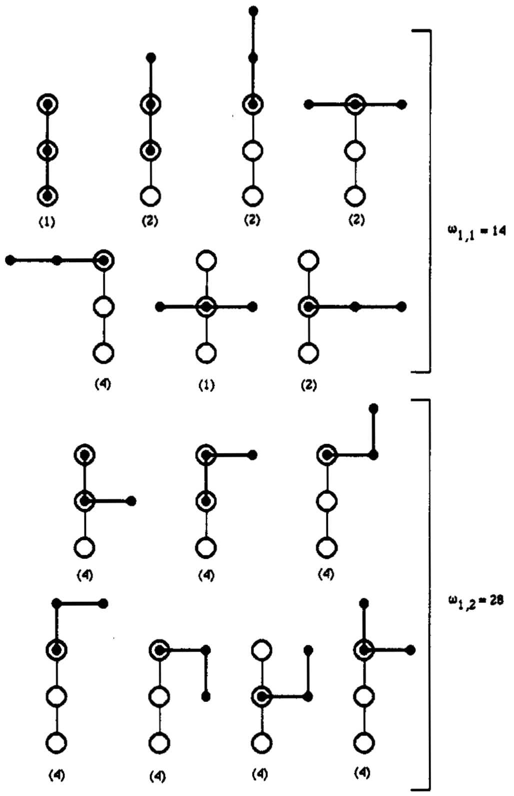

Figure 4. Enumeration of the lattice configurations whereby the adsorption of a trimer destroys the basic binding sites for trimers. The numbers in parentheses give the number of equivalent structures.

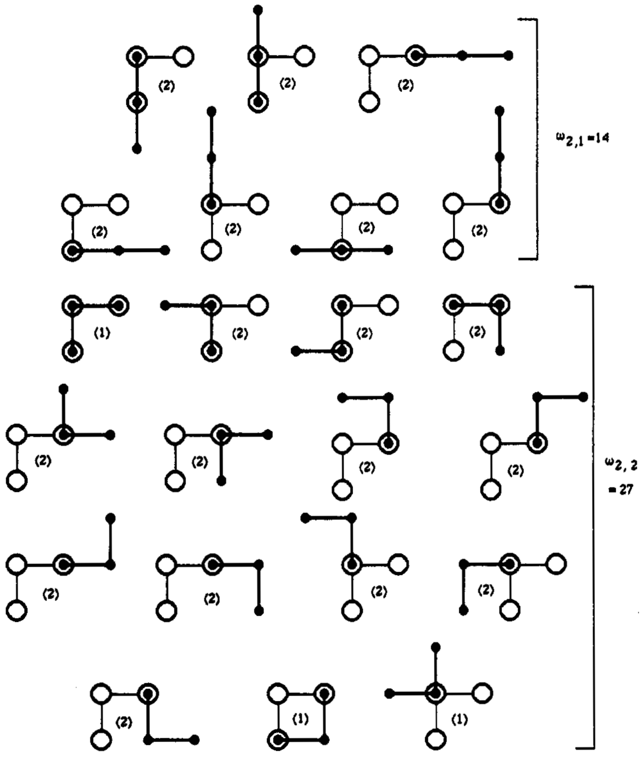

Figure 5. Continuation of Figure 4.

The general differential equation for the S_i can then be written as

$$dS_i/dt = -k_f z_p \sum_j \sum_k \omega_{ij}^{(k)} S_{ij}^{(k)} + k_b \rho_i^* \tag{2.3}$$

where $S_{ij}^{(k)}$ are the species shown in Figures 3 and 4 (the $\omega_{ij}^{(k)}$ are given in parentheses).

The differential equation for the net S is then

$$dS/dt = -k_f z_p \sum_i \omega_i \sum_j \sum_k \omega_{ij}^{(k)} S_{ij}^{(k)} + k_b \sum_i \omega_i \rho_i^* \tag{2.4}$$

The initial conditions are

$$S_i(t=0) = 1 \qquad S_{ij}^{(k)}(t=0) = 1 \qquad \rho_i^*(t=0) = 0 \tag{2.5}$$

Thus one has

$$(dS/dt)_0 = -k_f z_p \sum_i \omega_i \sum_j \omega_{ij} \tag{2.6}$$

where the quantity ω_{ij} is defined in (2.1).

If $\rho(t)$ is written as a power series in time

$$\rho(t) = \sum_{n=0}^{\infty} \rho^{(n)} t^n / n! \tag{2.7}$$

then (2.6) and (1.8) give (here we assume that z_p is constant for simplicity; we define $\kappa = k_f z_p$)

$$\rho^{(1)} = \kappa \sum_i \omega_i \qquad \rho^{(2)} = -\kappa k_b \sum_i \omega_i - \kappa^2 \sum_i \omega_i \sum_j \omega_{ij} \tag{2.8}$$

We emphasize that the above results are for the case of no surface diffusion and no conformational transitions on the surface (i.e., the polymers are frozen on the surface). We now show that the quantities in (2.8) are related to familiar quantities from equilibrium statistical mechanics.

3. Relation to Virial Coefficients

Using the notation of the previous paper, the conformational partition functions for one and two species are

$$Q_i = M\omega_i \qquad Q_{ij} = M\omega_i(\omega_j M - \omega_{ij}) \tag{3.1}$$

The quantity Q_i reflects the fact that there are M ways to place species i on the lattice with ω_i rotations and reflections at each site. With respect to Q_{ij}, $M\omega_i$ is the number of ways of placing the first molecule (in conformation i) on the lattice, and $(\omega_j M - \omega_{ij})$ is the number of ways of placing the second molecule (in conformation j) given the presence of the first molecule. The total partition functions (sums over all conformations) are (see eq 2.4 of paper 1)

$$Z_1 = \sum_i Q_i \qquad Z_2 = \frac{1}{2!} \sum_{i,j} Q_{ij} \tag{3.2}$$

Since the coefficients in the Mayer activity series (see eq 2.7 of paper 1), the b_l, are simply the part of the Z_l linear in M, one has

$$b_1 = \sum_i \omega_i \qquad b_2 = -\frac{1}{2} \sum_i \omega_i \sum_j \omega_{ij} \tag{3.3}$$

(We note that the b_l's given above are strictly not virial coefficients, as noted in section 6 of paper 1.) But the sums in (3.3) are the same as those in (2.5). Hence we have in general ($\kappa = k_f z_p$; z_p constant)

$$\rho^{(0)} = 0 \qquad \rho^{(1)} = \kappa b_1 \qquad \rho^{(2)} = 2\kappa^2 b_2 - \kappa k_b b_1 \tag{3.4}$$

The question now arises as to whether one can obtain a general recipe for determining $\rho^{(l)}$ as a function of b_l. We turn now to this task.

4. Kinetics from Equilibrium Quantities

To obtain a general equation relating kinetics to equilibrium quantities (b_l) we rewrite our basic kinetic equation as

$$d\rho/dt = k_f z_p S - k_b \rho \tag{4.1}$$

At equilibrium, the activity of the polymers on the lattice,

z, is related to the activity of the polymers in solution, z_p, by the relation (see the Appendix)

$$z = Kz_p \tag{4.2}$$

where K is the equilibrium constant for binding a polymer to the lattice surface

$$K = k_f/k_b \tag{4.3}$$

Thus at equilibrium one has the relation

$$S = \rho/z \tag{4.4}$$

This is a general relation for hard particle systems. Thus if we assume that we can use $z = z(\rho)$ as given by equilibrium statistical mechanics (i.e., use the assumption that the lattice is always in a state of internal equilibrium), then (4.4) gives a general way to determine S as a function of ρ.

In order to construct ρ/z we need the following standard relations (see paper 1, eqs 2.6, 3.12, and 4.9)

$$\Gamma = \sum_{l=1}^{\infty} b_l z^l \qquad \rho = \frac{\partial \Gamma}{\partial \ln z} = \sum_{l=1}^{\infty} l b_l z^l \qquad z = \sum_{l=1}^{\infty} a_l \rho^l \tag{4.5}$$

The first few a_l are (see paper 1, eq 4.9)

$$a_1 = b_1 \qquad a_2 = -2b_2/b_1 \qquad a_3 = 8b_2^2/b_1^5 - 3b_3/b_1^4 \tag{4.6}$$

One then has

$$\frac{\rho}{z} = \frac{\rho}{a_1\rho + a_2\rho^2 + a_3\rho^3 + \ldots} = \left(\frac{1}{a_1}\right) - \left(\frac{a_2}{a_1^2}\right)\rho + \left(\frac{a_2^2}{a_1^3} - \frac{a_3}{a_1^2}\right)\rho^2 + \ldots \tag{4.7}$$

Writing in general

$$\frac{\rho}{z} = \sum_{l=1}^{\infty} c_l \rho^l \tag{4.8}$$

then from (4.6) and (4.7) one has

$$c_0 = b_1 \qquad c_1 = 2b_2/b_1 \qquad c_2 = 3b_3/b_1^2 - 4b_2^2/b_1^3 \tag{4.9}$$

Our general differential equation is now an equation in terms of the single variable ρ

$$\mathrm{d}\rho/\mathrm{d}t = k_f z_p \sum_{l=0}^{\infty} c_l \rho^l - k_b \rho \tag{4.10}$$

If the power series expression of $\rho(t)$ of (2.7) is used, then (4.10) becomes a simple recursion relation for the $\rho^{(l)}$ starting with $\rho^{(0)} = 0$. Using (1.7) to express z_p as a function of ρ, one then obtains (with $\kappa = k_f C_p$)

$$\rho^{(0)} = 0$$

$$\rho^{(1)} = (\kappa)[b_1]$$

$$\rho^{(2)} = (\kappa^2)[2b_2 - cb_1^2] - (k_b\kappa)[b_1]$$

$$\rho^{(3)} = (\kappa^3)[6b_3 + (2b_2/b_1 - cb_1)^2 b_1 - 8b_2^2/b_1 - 4cb_2b_1] - (k_b\kappa^2)[4b_2 - cb_1^2] + (k_b^2\kappa)[b_1] \tag{4.11}$$

For the special case of constant polymer activity in solution ($c = 0$) the above relations become

$$\rho^{(0)} = 0$$

$$\rho^{(1)} = (\kappa)[b_1]$$

$$\rho^{(2)} = (\kappa^2)[2b_2] - (k_b\kappa)[b_1]$$

$$\rho^{(3)} = (\kappa^3)[6b_3 - 4b_2^2/b_1] - (k_b\kappa^2)[4b_2] + (k_b^2\kappa)[b_1] \tag{4.12}$$

If the binding is also irreversible ($k_b = 0$), then eqs 4.12 further simplify to

$$\rho^{(0)} = 0$$

$$\rho^{(1)} = b_1\kappa$$

$$\rho^{(2)} = -2b_2\kappa^2$$

$$\rho^{(3)} = (6b_3 - 4b_2^2/b_1)\kappa^3 \tag{4.13}$$

In a like manner one can determine as many $\rho^{(l)}$ coefficients in (2.7) as one has equilibrium b_l. One observes that $\rho^{(1)}$ and $\rho^{(2)}$ in (3.4) are exactly the same as those given in (4.12) (this would also be the case for the more general (4.11)). We recall that the coefficients in (3.4) were constructed by writing down the exact hierarchy of differential equations for the various binding sites assuming immobile polymers once bound, while (4.12) was constructed by using the assumption that internal equilibration, expressed by (4.7), holds at all times. Thus we have shown that the assumption of internal equilibration gives the first two derivatives of $\rho(t)$ exactly for the case of immobile bound polymers. We have explored in detail the nature of the assumption of internal equibration for the adsorption of hard particles (excluded volume only) with nearest-neighbor exclusion.[2] In that case the use of (4.7) gives the exact first three derivatives, i.e., $\rho^{(1)}$, $\rho^{(2)}$, and $\rho^{(3)}$, for the case of immobile bound particles. For the case of binding with nearest-neighbor attraction, the use of the assumption of internal equilibrium gives the first two derivatives exactly.[3] We have shown that for the case of the adsorption of dimers, the assumption of internal equilibration gives the first three derivatives exactly.[5]

The use of the assumption of internal equilibrium involves the approximation that the equlibrium relation of (4.7) holds as a function of time for immobile particles. Strictly, for true internal equilibrium the particles would in fact have to be infinitely mobile, both with respect to translation on the lattice and with respect to conformational interchange. We have studies the adsorption process in detail, including explicit surface diffusion, in order to understand the nature of the assumption of internal equilibrium.[2,3] The fact that we obtain at least two derivatives exactly for the immobile binding of polymers using the assumption of internal equilibration means that it is a fair approximation for the whole binding process since the limiting density will be given exactly and the first two derivatives are exact.

In our study[2] of hard particles with nearest-neighbor exclusion we have found that the assumption of internal equilibrium gives an upper bound for the rate of adsorption (it assumes an infinite rate of internal diffusion and hence is faster, with respect to higher derivatives, than the actual case of immobile molecules). In general for these systems, the assumption of internal equilibrium gives a very good

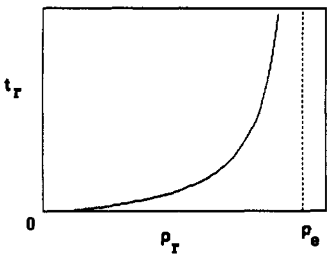

Figure 6. Illustration of time as a function of density as given in (5.8). The data shown represent a plot of (5.21) for $n = 7$.

representation of adsorption kinetics, except for at the very last stages of the process.

5. Time as a Function of Density. Discussion

Equation 2.7 gives ρ as a power series in time, which we can write as

$$\rho(t) = \alpha_1 t + \alpha_2 t^2 + \alpha_3 t^3 + ... \qquad (5.1)$$

where

$$\alpha_n = \rho^{(n)}/n! \qquad (5.2)$$

The coefficients α_n generally alternate in sign, making the use of truncated versions of (5.1) difficult to use. A more useful form[6] can be obtained by inverting (5.1) and considering time as a function of density

$$t = \beta_1\rho + \beta_2\rho^2 + \beta_3\rho^3 + ... \qquad (5.3)$$

where

$$\beta_1 = 1/\alpha_1 \qquad \beta_2 = -\alpha_2/\alpha_1^3 \qquad \beta_3 = 2\alpha_2^2/\alpha_1^5 - \alpha_3/\alpha_1^4 \qquad (5.4)$$

In general the coefficients β_n are all found to be positive and the radius of convergence of the ρ series is the equilibrium density, ρ_e (assuming that the binding is reversible). The general behavior of $t = t(\rho)$ for reversible binding is schematically shown in Figure 6.

The ratios of successive terms in the series give progressive estimates of the radius of convergence of the series, i.e.

$$r_n = \beta_n/\beta_{n-1} \rightarrow 1/\rho_e \qquad (5.5)$$

For our polymer model we do not know the equilibrium density as a function of activity accurately, since from paper 1 we know at most three terms in the $z = z(\rho)$ or $\rho = \rho(z)$ series. Thus, for illustrative purposes, we turn to the case of irreversible binding at constant polymer activity in solution. In this case, assuming internal equilibration, the radius of convergence of (5.3) will be the density of the close-packed lattice, i.e., $\rho_{max} = 1/n$. We assume that there is no equilibrium critical point at $\rho < \rho_{max}$ such as occurs in other hard-particle lattice gases, for example, as in the case of particles on the plane-square lattice with nearest-neighbor exclusion.[7] There is no obvious reason why the molecules should be forced to pick a particular sublattice at some critical value of the density in this model; for the case of dimers it is known exactly[8] that there are no singularities before ρ_{max}. If we did not make the assumption of internal equilibration, then the radius of convergence would be less than ρ_{max} since random irreversible placing of polymers on the surface would irreversibely lock some unoccuppied lattice sites into an inaccessible state.

Table I
The Quantities $\rho^{(1)}$, $\rho^{(2)}$, and $\rho^{(3)}$ of Equation 4.13 as a Function of Chain Length, n, for Irreversible Binding with Constant z_p[a]

n	$\rho^{(1)}/\kappa$	$\rho^{(2)}/\kappa^2$	$\rho^{(3)}/\kappa^3$
2	2	−14	134
3	6	−248	14613(1/3)
4	18	−3 446	9.578×10^5
5	50	−37 768	4.119×10^7
6	142	−399 846	1.698×10^9
7	390	−3 827 104	5.832×10^{10}
8	1086	−36 169 622	

[a] These quantities were constructed by using the b_l data from Table II in paper 1.

Table II
The Quantities ϕ_2 and ϕ_3 of Equation 5.9 as a Function of Chain Length, n, for Irreversible Binding with Constant Activity z_p

n	ϕ_2	ϕ_3	n	ϕ_2	ϕ_3
2	0.8750	0.8333	6	1.6526	2.7154
3	1.1481	1.3836	7	1.7973	3.1160
4	1.3295	1.8243	8	1.9167	
5	1.5107	2.3677			

It is convenient to scale the density relative to the maximum possible density

$$\rho_r = \rho/\rho_{max} = n\rho \qquad (5.6)$$

and, for purposes of comparing the series for different chain lengths, we scale the time so that

$$dt_r/d\rho_r = 1 \qquad (5.7)$$

that is, the initial slope is unity for all chain lengths. One then has

$$t_r = \phi_1\rho_r + \phi_2\rho_r^{\ 2} + \phi_3\rho_r^{\ 3} + ... \qquad (5.8)$$

where (with $\kappa = k_f z_p$)

$$\phi_m = \frac{\beta_m}{\beta_1}\left(\frac{1}{n}\right)^{m-1} \qquad t_r = \left(\frac{n}{\beta_1}\right)t = n\kappa b_1 \qquad (5.9)$$

or

$$\phi_1 = 1$$

$$\phi_2 = \frac{b_2}{nb_1^{\ 2}}$$

$$\phi_3 = \frac{8}{3}\left(\frac{b_2}{nb_1^{\ 2}}\right)^2 - \frac{b_3}{n^2b_1^{\ 3}} = \frac{8}{3}\phi_2^{\ 2} - \frac{b_3}{n^2b_1^{\ 3}} \qquad (5.10)$$

The ϕ's turn out to be independent of κ.

For the case of irreversible binding with constant polymer activity in solution $\rho^{(l)}$ and ϕ_l defined above are given in Table II as a function of n. These quantities were constructed using the b_n given in Table II in paper 1. One sees that while $\rho^{(l)}$'s are large cumbersome numbers, ϕ_l's are small and nicely behaved. One observes that there is a modest increase in ϕ_2 and ϕ_3 as a function of n. Assuming the forms

$$\phi_2 \sim n^{\delta_2} \qquad \phi_3 \sim n^{\delta_3} \qquad (5.11)$$

and using eq 3.5 of Paper 1, one obtains the estimates of the exponents δ_2 and δ_3 given in Table III.

The ϕ values in Table II indicate that the relaxation process for the binding of polymers is much slower than exponential decay. In our relative units, if the relaxation were simple exponential decay, one would have

$$(1 - \rho_r) = \exp(-t_r) \qquad (5.12)$$

or

$$t_r = -\ln(1 - \rho_r) = \rho_r + (1/2)\rho_r^{\ 2} + (1/3)\rho_r^{\ 3} + ... \qquad (5.13)$$

Table III
The Exponents δ_1 and δ_2 of Equation 5.11 Obtained from the Values of ϕ_2 and ϕ_3 Given in Table II[a]

n	δ_1	δ_2	n	δ_1	δ_2
3	0.670	1.250	6	0.492	0.752
4	0.510	0.961	7	0.545	0.893
5	0.573	1.168	8	0.482	

[a] The numbers were obtained by using eq 3.5 of paper 1; $n_2 = n$ and $n_1 = n - 1$.

Since from Table II

$$\phi_2 > 1/2 \qquad \phi_3 > 1/3 \tag{5.14}$$

the adsorption process is clearly slower than simple exponential decay and gets slower with larger chain length.

Recently Pefferkorn et al.[9] studied the kinetics of the adsorption of polymers to a planar surface. They interpreted their data in terms of a rate constant for adsorption that was a function of the surface coverage. We can cast our results in that form as follows. Using our relative variables t_r and ρ_r, we write

$$(1 - \rho_r) = \exp[-k(\rho_r)t_r] \tag{5.15}$$

which defines the density-dependent rate parameter $k(\rho_r)$. Then using (5.8) and (5.13), one obtains

$$k(\rho_r) = 1 - (\phi_2 - 1/2)\rho_r - (\phi_3 + \phi_2/2 - \phi_2^2 - 1/3)\rho_r^2 + \ldots \tag{5.16}$$

Using the data of Table II (for the case of irreversible binding with constant activity), one has

$$(n = 2) \qquad k(\rho_r) = 1 - 0.375\rho_r - 0.172\rho_r^2 + \ldots$$

$$(n = 7) \qquad k(\rho_r) = 1 - 1.297\rho_r - 0.452\rho_r^2 + \ldots \tag{5.17}$$

If the relaxation were simple exponential decay, then $k = 1$ for all ρ_r in the range 0–1. Since one must have $k > 0$, the rate of dropoff of k with ρ_r must level off. Lacking information about the limit $k(\rho_r{=}1)$, we can take $k(\rho_r{=}1) \approx 0$. We can enforce this limit by incorporating an addition term in the truncated series (5.17) that makes $k(\rho_r{=}1) = 0$. Thus we have, for example

$$(n = 2) \qquad k(\rho_r) = 1 - 0.375\rho_r - 0.172\rho_r^2 - 0.453\rho_r^3$$

$$(n = 7) \qquad k(\rho_r) = 1 - 1.297\rho_r - 0.452\rho_r^2 + 0.749\rho_r^3 \tag{5.18}$$

The above two functions are shown in Figure 7. Clearly the adsorption process is very much slower than exponential decay (where one would have $k = 1$ for all ρ_r), a result of the extensive excluded volume effect of the adsorbed polymer molecules. For the case of the irreversible binding of dimers with internal equilibration, one knows[5] that in fact k does equal zero at $\rho_r = 1$.

Clearly one could make the polymer adsorption model treated here more complicated by including attractive interactions, both intra- and intermolecular, between the polymer molecules. One could also allow the polymers to adsorb in a less neat fashion than used here by permitting chains to cross (with a bulge) on the surface. All of these features could be incorporated into the model simply by formulating the appropriate b_l. Our main point here is that one can use the techniques of equilibrium statistical mechanics to obtain information about the kinetics of adsorption.

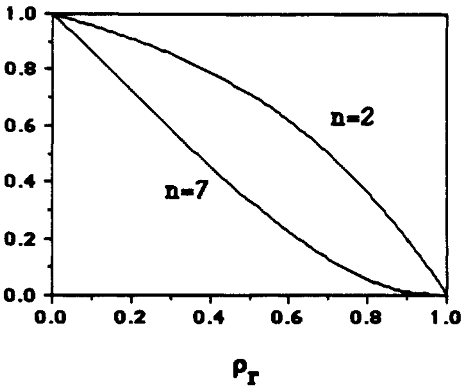

Figure 7. Variation of the density-dependent rate constant $k(\rho_r)$ defined in (5.15) as given by (5.18) for $n = 2$ and 7. If the adsorption process were described by exponential decay, then $k = 1$ for all ρ_r.

Appendix

In this Appendix we review some basic relations concerning the activity that are important for the treatment of the kinetics of adsorption. We begin with the fundamental equation for the Gibbs free energy at constant N (number of molecules)

$$\mathrm{d}G - V\,\mathrm{d}p \tag{A-1}$$

Recalling that for a single-component system the chemical potential is given by

$$\mu = G/N \tag{A-2}$$

we divide both sides of (A-1) by N and obtain an equation for μ in terms of the integration constant $\mu^0(T)$ (where $\beta = 1/kT$ and $\rho = N/V$)

$$\beta\mu = \beta\mu^0(T) + \int \frac{1}{\rho}\frac{\partial \beta p}{\partial \rho}\,\mathrm{d}\rho \tag{A-3}$$

Expressing the equation of state as a virial (density) series

$$\beta p = \rho + 3B_2\rho^2 + B_3\rho^3 + \ldots \tag{A-4}$$

(A-3) becomes

$$\beta\mu = \beta\mu^0 + \ln\rho + \ln\gamma \tag{A-5}$$

where

$$\ln\gamma = 2B_{2\rho} + (3/2)B_3\rho^3 + \ldots \tag{A-6}$$

We define the activity as

$$z = \rho\gamma \tag{A-7}$$

Thus in general (not just for ideal systems) we have

$$\beta\mu = \beta\mu^0 + \ln z \tag{A-8}$$

If we now consider a solvent with solute molecules that can adsorb to a surface (lattice), one has for the chemical potentials of the molecules in solution and adsorbed to the lattice

$$\beta\mu_{\mathrm{sol}} = \beta\mu_{\mathrm{sol}}^{0} + \ln z_{\mathrm{sol}} = -\ln q_{\mathrm{sol}} + \ln z_{\mathrm{sol}}$$

$$\beta\mu_{\mathrm{lattice}} = \beta\mu_{\mathrm{lattice}}^{0} + \ln z_{\mathrm{lattice}} = -\ln q_{\mathrm{lattice}} + \ln z_{\mathrm{lattice}} \tag{A-9}$$

where q_{sol} and q_{lattice} are the appropriate molecular partition functions (giving the integration constant $\beta\mu^0$). At equilibrium

$$\beta\mu_{\mathrm{sol}} = \beta\mu_{\mathrm{lattice}} \tag{A-10}$$

or

$$z_{\mathrm{sol}}/q_{\mathrm{sol}} = z_{\mathrm{lattice}}/q_{\mathrm{lattice}} \tag{A-11}$$

or

$$Kz_{\mathrm{sol}} = z_{\mathrm{lattice}} \tag{A-12}$$

where the equilibrium constant K for binding is given by

$$K = q_{\mathrm{lattice}}/q_{\mathrm{sol}} \tag{A-13}$$

The basic differential equation for binding is

$$\mathrm{d}\rho/\mathrm{d}t = k_{\mathrm{f}}z_{\mathrm{sol}}S - k_{\mathrm{b}}\rho \tag{A-14}$$

where S is the density of the appropriate binding site. At equilibrium, $\mathrm{d}\rho/\mathrm{d}t = 0$ and one has (using the alternative relation for the equilibrium constant, $K = k_{\mathrm{f}}/k_{\mathrm{b}}$)

$$S = \rho/Kz_{\mathrm{sol}} \tag{A-15}$$

or, using (A-12)

$$S = \rho/z_{\mathrm{lattice}} \tag{A-16}$$

We can now drop all reference to the solution and take z_{lattice} simply as the activity of the lattice gas, giving the general relation for hard particle systems

$$S = \rho/z \tag{A-17}$$

For molecules with many conformations and orientations, the quantities S and ρ have the interpretations (using the symbols defined in the text)

$$S = \sum \omega_i S_i \qquad \rho = \sum \omega_i \rho_i^* \tag{A-18}$$

The symbols S_i etc. refer to the probabilities of specific chunks of lattice sites. Thus for the dimer S_1 is the probability of having two empty nearest-neighbor lattice sites in a particular orientation on the lattice. These probabilities are normalized in the sense that the sum of the probabities of all possible states of occupancy of the same lattice chunk must add up to one (some of the states may be forbidden by excluded volume). For the example of the dimer, one has

$$p_{00} + p_{01} + p_{10} + p_{11} = 1 \tag{A-19}$$

where zero and one indicate respectively unoccupied and occupied lattice sites. In our example, $S_1 = p_{00}$. At time equal zero we start with an empty lattice, hence $p_{00}(0) = S_1(0) = 1$ and $p_{01}(0) = p_{10}(0) = p_{11}(0) = 0$.

References and Notes

(1) Poland, D. *Macromolecules*, preceding paper in this issue.
(2) Poland, D. *J. Stat. Phys.* **1989**, *55*, 389.
(3) Poland, D. *J. Stat. Phys.* **1990**, *59*, 935.
(4) Poland, D. *J. Stat. Phys.* **1990**, *61*, 765. Concerning the general use of equilibrium virial coefficients in kinetics.
(5) Poland, D., work in progress.
(6) Poland, D. *J. Comp. Chem.* **1990**, *11*, 382.
(7) Guant, D. S.; Fisher, M. E. *J. Chem. Phys.* **1965**, *43*, 2840.
(8) Heilmann, O. J.; Lieb, E. H. *Phys. Rev. Lett.* **1970**, *24*, 1412.
(9) Pefferkorn, A.; Haouam, A.; Varoqui, R. *Macromolecules* **1988**, *21*, 2111.