Statistical Theory of the Adsorption of Interacting Chain Molecules. 1. Partition Function, Segment Density Distribution, and Adsorption Isotherms

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Statistical Theory of the Adsorption of Interacting Chain Molecules. 1. Partition Function, Segment Density Distribution, and Adsorption Isotherms

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We present a general theory for polymer adsorption using a quasi-crystalline lattice model. The partition function for a mixture of polymer chains and solvent molecules near an interface is evaluated by adopting the Bragg–Williams approximation of random mixing within each layer parallel to the surface. The interaction between segments and solvent molecules is taken into account by use of the Flory–Huggins parameter χ; that between segments and the interface is described in terms of the differential adsorption energy parameter χ_s. No approximation was made about an equal contribution of all the segments of a chain to the segment density in each layer. By differentiating the partition function with respect to the number of chains having a particular conformation an expression is obtained that gives the numbers of chains in each conformation in equilibrium. Thus also the train, loop, and tail size distribution can be computed. Calculations are carried out numerically by a modified matrix procedure as introduced by DiMarzio and Rubin. Computations for chains containing up to 1000 segments are possible. Data for the adsorbed amount Γ, the surface coverage θ, and the bound fraction $p = \theta/\Gamma$ are given as a function of χ_s, the bulk solution volume fraction ϕ_*, and the chain length r for two χ values. The results are in broad agreement with earlier theories, although typical differences occur. Close to the surface the segment density decays roughly exponentially with increasing distance from the surface, but at larger distances the decay is much slower. This is related to the fact that a considerable fraction of the adsorbed segments is present in the form of long dangling tails, even for chains as long as $r = 1000$. In previous theories the effect of tails was usually neglected. Yet the occurrence of tails is important for many practical applications. Our theory can be easily extended to polymer in a gap between two plates (relevant for colloidal stability) and to copolymers.

I. Introduction

The adsorption of polymers at interfaces is an important phenomenon, both from a theoretical point of view and for numerous practical applications. One of the areas where polymer adsorption plays a role is in colloid science, since many colloidal systems are stabilized or destabilized by polymeric additives. In these cases, not only the adsorbed amount is an important parameter, but also the way in which the polymer segments are distributed in the vicinity of a surface. An adsorbed polymer molecule generally exists of *trains* (sequences in actual contact with the surface), *loops* (stretches of segments in the solution of which both ends are on the surface), and *tails* (at the ends of the chain with only one side fixed on the surface). If two surfaces are present at relatively short separations, *bridges* (of which the ends are adsorbed on different surfaces) may also occur. The properties of systems in which polymer is present depend strongly on the length and distribution of trains, loops, tails, and bridges.

Many of the older theories[1-6] on polymer adsorption treat the case of an isolated chain on a surface. These treatments neglect the interaction between the segments and have, therefore, little relevance for practical systems, since even in very dilute solutions the segment concen-

tration near the surface may be very high. Other theories[7,8] account for the interaction between chain segments but make specific assumptions about the segment distribution near the surface which are not completely warranted, such as the presence of a surface phase with only adsorbed molecules[7] or the neglect of tails.[8] For oligomers up to four segments a sophisticated theory has been presented[9] but its application to real polymer molecules is impossible due to the tremendous computational difficulties involved. The most comprehensive theory for polymer adsorption as yet has been given by Roe,[10] although here also a simplifying assumption is made, namely, that each of the segments of a chain gives the same contribution to the segment density at any distance from the surface. Roe arrives at the segment density profile near the surface, but does not calculate loop, train, and tail size distributions. Recently, Helfand[11] has shown that Roe's theory is also incorrect on another point, since the inversion symmetry for chain conformations is not properly taken into account. Helfand corrects this by introducing the so-called flux constraint, but his calculations apply only to infinite chain lengths.

Less work has been done on the problem of polymer between two plates. DiMarzio and Rubin[12] give an elegant

matrix procedure for this case, but are not able to incorporate the polymer–solvent interaction. In two other recent theories[13,14] this was done for terminally adsorbing polymers. The paper by Levine et al.[14] can be considered as a combination of the matrix method of DiMarzio and Rubin and the self-consistent field theory.[15] However, here also the loop, train, and tail size distributions were not calculated.

In this series of articles, we describe how the probability of any chain conformation in a lattice adjoining one or two interfaces is found from the partition function for the mixture of polymer chains and solvent molecules in the lattice. The crucial difference with the theories of Roe and Helfand is that the partition function is not written in terms of concentrations of individual segments, but in terms of concentrations of chain conformations; throughout the derivation the chains are treated as connected sequences of segments. The interaction between segments and solvent molecules is taken into account by using the Bragg–Williams approximation of random mixing within each layer parallel to the surface, in a way similar to the well-known Flory–Huggins theory for moderately concentrated polymer solutions. The segment density near the interface is found from a modification of DiMarzio and Rubin's matrix formalism.[12] Since the probability of each conformation can be calculated, the distribution of trains, loops, and tails (and for the two-plate problem also bridges) can be found.

In this first paper we derive the adsorption isotherms and the segment density distribution for polymer adsorbing on one plate. In a second article, the loop, train, and tail size distribution will be treated in more detail. The general trends are in agreement with earlier theories,[7-10] but an important difference occurs concerning the segment density at relatively large distances from the surface. In this region, the main contribution to the segment concentration appears to be due to the presence of long dangling tails. This outcome was not found by former theories and may be considered as one of the most interesting results of the present treatment. It is certainly very important in the stabilization and flocculation of colloidal particles by polymers.

In a subsequent publication we shall treat the problem of polymer between two plates which is, among other applications, relevant for flocculation. Our method can easily be extended to (block and random) copolymers, to heterogeneous surfaces, etc. In later contributions these aspects will be dealt with.

II. Theory

A. Formulation of the Model. We consider a mixture of n polymer molecules, each consisting of r segments, and n^0 solvent molecules distributed over a lattice such that each solvent molecule occupies one lattice site. In the present paper, we consider only homopolymers of which each segment has the same size as a solvent molecule and also occupies one lattice site. The lattice adjoins an adsorbing surface and is divided into M layers of sites parallel to the surface, numbered $i = 1, 2, ..., M$. Each layer contains L lattice sites. Therefore

$$n^0 + rn = ML \qquad (1)$$

The volume fractions of solvent in layer i are indicated by ϕ_i^0 and ϕ_i, respectively, and are given by

$$\phi_i^0 = n_i^0/L \qquad \phi_i = n_i/L \qquad (2)$$

where n_i^0 and n_i are the numbers of solvent molecules and polymer segments in layer i. Far from the surface these volume fractions approach the equilibrium bulk volume
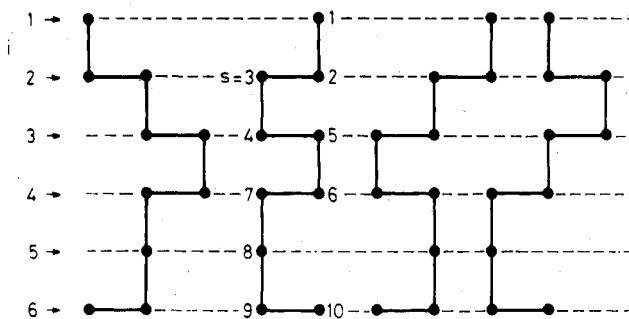

Figure 1. Some examples of different arrangements for a chain of 10 segments ($r = 10$). All the indicated arrangements belong to the conformation (1,1)(2,2)(3,2)(4,3)(5,3)(6,4)(7,4)(8,5)(9,6)(10,6). This example applies to a simple square two-dimensional lattice ($z = 4$, λ_1 = 1/4, λ_0 = 1/2). The number of different arrangements in the given conformation is $z^9\lambda_1^5\lambda_0^4 = 16$. Only four of them are indicated.

fractions ϕ_*^0 and ϕ_*, respectively.

If z is the coordination number of the lattice, a lattice site in layer i has z nearest neighbors, of which a fraction λ_{j-i} is in layer j. Thus, $\lambda_{j-i} = \lambda_0$ if $j = i$ and $\lambda_{j-i} = \lambda_1 = \lambda_{-1}$ if $j = i \pm 1$. As there are no nearest neighbors in nonadjacent layers, $\lambda_{j-i} = 0$ if $|j - i| \geq 2$, and we may write

$$\sum_{j=1}^{M} \lambda_{j-i} = 1 \qquad 1 < i < M \qquad (3)$$

For the two boundary layers ($i = 1$ and $i = M$), a correction has to be applied since there is only one adjacent layer, and a segment has only $z(\lambda_0 + \lambda_1) = z(1 - \lambda_1)$ nearest neighbors. Thus

$$\sum_{j=1}^{M} \lambda_{j-i} = 1 - \lambda_1 \qquad i = 1, M \qquad (4)$$

The segments of a polymer chain are labeled $s = 1, 2, ..., r$. Each chain can assume a large number of possible conformations in the lattice. We characterize a *conformation* by defining the layer numbers in which each of the successive chain segments find themselves. We denote such a conformation by

$$(1,i)(2,j)(3,k)...(r - 1,l)(r,m)$$

indicating that the first segment is in i, the second in j, the third in k, etc.

We have to realize that a conformation defined in this way is actually a set of many different arrangements. If segment s is placed in i and segment $s + 1$ in j, the number of different positions of segment $s + 1$ with respect to segment s is $z\lambda_0$ if $j = i$ and $z\lambda_1$ if $j = i \pm 1$. A dimer with conformation $(1,i)(2,j)$ can assume $Lz\lambda_{j-i}$ different positions; a trimer with conformation $(1,i)(2,j)(3,k)$ can be arranged in $Lz^2\lambda_{j-i}\lambda_{k-j}$ different ways, at least if backfolding of the chain is allowed. For example, in a simple cubic lattice ($z\lambda_1 = 1$) backfolding occurs in the conformation $(1,2)(2,3)(3,2)$. In section II.D, we shall correct partly for this backfolding effect. Figure 1 illustrates for a simple case some different arrangements in a conformation.

We label the different conformations by c, d, ... If conformation c for an r-mer is characterized by the sequence given above, the number of different arrangements in this conformation is given by $Lz^{r-1}\lambda_{j-i}\lambda_{k-j}...\lambda_{m-l}$. More generally, we can write for the number of arrangements $L\omega_c z^{r-1}$ where ω_c is given by

$$\omega_c = \prod_{s=1}^{r-1} (\lambda_{s,s+1})_c \qquad (5)$$

Here $(\lambda_{s,s+1})_c = \lambda_0$ if, in conformation c, segments s and $s + 1$ are in the same layer, and $(\lambda_{s,s+1})_c = \lambda_1$ if these two segments are in neighboring layers. Since z^{r-1} is the

number of arrangements for a chain in bulk polymer, of which one of the segments is fixed, ω_c may be considered as the ratio between the number of arrangements of conformation c and that in bulk polymer.

If the number of polymer molecules in conformation c is n_c, we have

$$n = \sum_c n_c \qquad (6)$$

where the summation extends over all possible conformations c. Obviously, the number of terms in the summation of eq 6 increases sharply with r. In a few cases we will consider all the possible arrangements of only a part of the chain. Then, we will use the symbol $\omega_c(s,t)$ to indicate the relative number of arrangements of the chain part from segment s up to and including segment t. Similarly, a summation $\sum_{c(s,t)}$ specifies that all the possible conformations of that part of the chain have to be taken into account. In this terminology, ω_c in (5) could be written as $\omega_c(1,r)$ and $\sum_c$ in (6) as $\sum_{c(1,r)}$.

For the further elaboration it is expedient to introduce the symbol $r_{i,c}$ for the number of segments that conformation c has in layer i. Then the number of segments in layer i is given by

$$n_i = \sum_c r_{i,c} n_c \qquad (7)$$

In the following sections we need a symbol to indicate the layer number in which segment s of conformation c finds itself. For this we use $k(s,c)$. Here, k is one of the layer numbers 1, 2, ..., M and is completely determined if conformation c is specified.

One remark on the use of conformations as defined above is in order. This definition corresponds to one particular way of grouping the possible arrangements of individual chains in a set. Other ways of grouping are, in principle, possible. Also, a procedure could be used in which the individual chain arrangements are not combined in sets but are all treated separately. It is easily proven that, although the partition function to be derived below is slightly changed, the equations obtained after maximization of the partition function are identical. Therefore, the grouping of chain arrangements in conformations as defined above is only a matter of convenience.

B. Partition Function. Roe[10] gives an approximate expression for the canonical partition function $Q(M,L,T,\{n_i^0\})$ for a given concentration profile $\{n_i^0\}$ of solvent molecules in a lattice of M layers with L lattice sites each. From this partition function, the equilibrium distribution of solvent molecules and thus also the overall distribution of polymer segments can be derived. Roe made no attempt to calculate the distribution of trains, loops, and tails.

Roe's approach involves the assumption that the distribution of a polymer segment does not depend on its ranking number s. The contribution of *each* of the r chain segments to the segment concentration ϕ_i in each layer is considered to be equal to ϕ_i/r. This is correct in bulk but not near an interface, because the interface imposes restrictions which are not necessarily the same for end and inner segments. As Helfand[11] has shown, Roe's derivation contains another error because the inversion symmetry is not obeyed. This is the requirement that conformation c, defined as $(1,i)(2,j)...(s,k)...(r,l)$, should have the same probability as the inverted conformation c′, characterized by the sequence $(1,l)...(r-s+1,k)...(r-1,j)(r,i)$. Helfand maintains this symmetry by introducing an extra constraint, the flux constraint. His results apply only to infinitely high chain lengths. The flux constraint is only necessary if the partition function is written in terms of, and maximized with respect to, *the concentrations of*

individual segments in each layer. It may be considered as a correction which is necessary to account fully for the connected nature of the segments in a chain.

An alternative derivation is possible if the partition function is maximized with respect to the numbers of polymer chains in each conformation, i.e., with respect to *concentrations of chains in each conformation.* This has the additional advantage of giving immediately the probability of every chain conformation in the equilibrium situation, so that the train, loop, and tail size distribution can be easily evaluated. Moreover, as will be shown below, the inversion symmetry is an automatic result of this approach. Thus, we want the canonical partition function $Q(M,L,T,\{n_c\})$ for an arbitrary but specified set of conformations $\{n_c\}$. We have to realize that a given overall segment distribution can be the result of a great number of different combinations of trains, loops, and tails.

We now give a derivation of $Q(M,L,T,\{n_c\})$. Since the numbers of chains in each conformation and thus the numbers of solvent molecules in each layer are specified, the energy U of the system for each of the possible ways of arrangement is the same, at least if we adopt the Bragg–Williams approximation. Therefore, the partition function can be written as the product of a combinatory factor (representing the configurational entropy) and $\exp(-U/kT)$. In accordance with Flory[16] and Roe[10] we take as the reference state disoriented bulk polymer and pure solvent. Then

$$Q(M,L,T,\{n_c\}) = \frac{\Omega}{\Omega^+} e^{-U/kT} \qquad (8)$$

Here Ω is the number of ways of arranging n_c, n_d, n_e, ... polymer molecules in specified conformations, and n_1^0, ...n_i^0, ...n_M^0 solvent molecules over M distinguishable layers of L lattice sites each. Ω^+ is the number of ways of arranging n polymer chains over nr lattice sites in amorphous bulk polymer.

The combinatory factor Ω has to be evaluated according to the assigned distribution of conformations $\{n_c\}$. Naturally, if this set of conformations $\{n_c\}$ is specified, the concentration profile $\{n_i\}$ is completely determined.

We use the Bragg–Williams approximation of random mixing within each layer. This implies that the polymer segments in each layer are considered to be randomly distributed over the L lattice sites. The number of ways of placing a chain in conformation c in the empty lattice is $L\omega_c z^{r-1}$ (see eq 5). If part of the lattice sites is already occupied, a chain can only be placed if all the appropriate sites are vacant. Then we have to apply r correction factors, one for each of the chain segments. The correction factor for each segment is the vacancy probability of the site to be occupied. According to the Bragg–Williams approximation, we assume that all sites in layer i have the same vacancy probability, equal to $1 - \nu_i/L$, where ν_i is the number of previously occupied lattice sites in layer i. Obviously, $\nu_i = 0$ for an empty layer. The number of possibilities of placing one chain in conformation c can now be written as $L\omega_c z^{r-1}\prod_{s=1}^r(1 - \nu_{k(s,c)}/L) = \omega_c(z/L)^{r-1}\prod_{s=1}^r(L - \nu_{k(s,c)})$, where $\nu_{k(s,c)}$ is the number of previously occupied sites in the layer where segment s of conformation c is placed. For example, if conformation c of a hexamer is given by $(1,i)(2,j)(3,i)(4,j)(5,k)(6,j)$, $\omega_c = \lambda_1^5$ and the number of possibilities of placing this conformation in a lattice where a_i, a_j, and a_k lattice sites in the layers i, j, and k are already occupied is $(\lambda_1 z/L)^5(L - a_i)(L - a_j)(L - a_i - 1)(L - a_j - 1)(L - a_k)(L - a_j - 2)$. Generally, since $r_{i,c}$ segments are placed in layer i, this layer contributes $r_{i,c}$ factors, namely, $(L - a_i)(L - a_i - 1)(L - a_i - 2)...(L - a_i - r_{i,c} + 1)$, to the multiple product $\prod_{s=1}^r(L - \nu_{k(s,c)})$. The product over

the segment numbers can thus be replaced by a product over the layer numbers. The number of arrangements ω of placing the first chain (in conformation c) in the empty lattice ($a_i = 0$ for all i) becomes

$$\omega = \omega_c (z/L)^{r-1} \prod_{i=1}^{M} \prod_{\nu_i=0}^{r_{i,c}-1} (L - \nu_i) \ . \tag{9}$$

where layers in which conformation c has no segments (thus for which $r_{i,c} = 0$) do not contribute to ω.

Placing all the n_c chains of conformation c gives a factor $\omega_c^{n_c}(z/L)^{(r-1)n_c}$ in (9) while the multiplication extends up to $\nu_i = n_c r_{i,c} - 1$. Similarly, the number of arrangements for $n = \sum_c n_c$ chains is

$$\omega(n) = (z/L)^{(r-1)n} \prod_c \omega_c^{n_c} \prod_{i=1}^{M} \prod_{\nu_i=0}^{n_i-1} (L - \nu_i) \tag{10}$$

because $n_i = \sum_c r_{i,c} n_c$ segments are placed in each layer. Next, solvent molecules have to be arranged over the $L - n_i$ remaining lattice sites, giving for each layer $\prod_{\nu_i=n_i}^{L-1}(L - \nu_i)$ possibilities. Thus, we find for Ω the simple expression

$$\Omega = (L!)^M (z/L)^{(r-1)n} \prod_c \frac{\omega_c^{n_c}}{n_c!} \prod_{i=1}^{M} \frac{1}{n_i^0!} \tag{11}$$

since $\prod_{i=1}^{M} L! = (L!)^M$. The factorials $n_c!$ and $n_i^0!$ in (11) correct for the indistinguishability of the n_c chains in each conformation c and of solvent molecules within each layer.

It may be noted that the order of placing chains and solvent molecules is irrelevant for the final result. Similarly, it does not matter which of the r chain segments of a chain is placed first.

The combinatory factor Ω^+ has been derived by Flory[16] and can be written as

$$\Omega^+ = \frac{(rn)!}{n!}(z/rn)^{(r-1)n} \tag{12}$$

This combinatory factor can also be found by a procedure similar to the derivation of our eq 11. In the bulk all the layers i are identical, so that the distinction in lattice layers is irrelevant. Since rn is the total number of (equivalent) lattice sites in bulk polymer, the factor $(L!)^M$ in (11) has to be replaced by $(rn)!$ and the factor $L^{(r-1)n}$ by $(rn)^{(r-1)n}$. Moreover, all possible conformations are equally probable, and we can group them together in only one conformation. Substitution of $n_c = n$, $\omega_c = 1$, and $n_i^0 = 0$ in (11) gives the Flory expression (eq 12), demonstrating that our eq 11 is in complete agreement with earlier theories.

Combination of (11) and (12) gives for the entropy part of ln Q:

$$\ln \Omega/\Omega^+ = ML \ln L - \sum_c n_c \ln n_c/\omega_c - \sum_i n_i^0 \ln n_i^0 -$$
$$n \ln r - (r - 1)n \ln L \tag{13}$$

if Stirling's approximation for the factorials is applied.

The energy of the system contains a contribution due to the adsorption energy and a mixing term originating from the polymer–solvent interaction. We assume that in both cases only nearest-neighbor interactions are involved. The mixing term depends on the number of contacts between segments and solvent molecules. Each solvent molecule in layer i has $z\lambda_{j-i}$ contacts in layer j, a fraction ϕ_j of which are with polymer segments, according to the Bragg–Williams approximation. Since a site in i has neighbors in the layers $j = i - 1, i, i + 1$ the number of unlike contacts per solvent molecule in i is $z\sum_{j=1}^{M}\lambda_{j-i}\phi_j$. The total number of contacts is found by multiplying with n_i^0 and summing over all layers i. Thus, the total number of contacts of solvent molecules with segments is $z\sum_{i=1}^{M}n_i^0\langle\phi_i\rangle$ and the (equal) number of segment–solvent

molecule contacts is $z\sum_{i=1}^{M}n_i\langle\phi_i^0\rangle$, where the *site volume fractions* $\langle\phi_i\rangle$ for segments and $\langle\phi_i^0\rangle$ for solvent molecules are defined as

$$\langle\phi_i\rangle = \sum_{j=1}^{M} \lambda_{j-i}\phi_j \qquad \langle\phi_i^0\rangle = \sum_{j=1}^{M} \lambda_{j-i}\phi_j^0 \tag{14}$$

In the bulk solution $\langle\phi_*\rangle = \phi_*$ and $\langle\phi_*^0\rangle = \phi_*^0$. For $1 < i < M$, $\langle\phi_i\rangle + \langle\phi_i^0\rangle = 1$; for $i = 1$ and $i = M$, $\langle\phi_i\rangle + \langle\phi_i^0\rangle = 1 - \lambda_1$ (compare eq 4).

Using the familiar Flory–Huggins polymer solvent interaction parameter,[16] we can write for the energy part of ln Q:

$$U = n_1 u_s + n_1^0 u_s^0 + kT\chi \sum_{i=1}^{M} n_i^0 \langle\phi_i\rangle \tag{15}$$

In this equation, u_s and u_s^0 are the adsorption energies of a segment and a solvent molecule, respectively. They represent the energy change corresponding to the transfer of a segment (or solvent molecule) from bulk polymer (or solvent) to the surface. Equation 15 has also been given by Roe.[10]

It may be noted here that the energy terms in eq 15 also contain the thermal entropy, i.e., the additive part of the entropy proportional to the number of segments or solvent molecules. This thermal entropy includes vibrational and rotational contributions; the adsorption energy u_s may contain entropy terms due to orientation of solvent molecules near the surface (hydrophobic bonding). In this sense, the energy terms u_s, u_s^0, and $kT\chi$ may be considered as free energies. Obviously, the configurational part of the entropy is accounted for in ln Ω/Ω^+.

C. Conformation Probability. Equations 13 and 15 give the logarithm of the partition function at a given distribution of conformations $\{n_c\}$, which in general does not correspond to the equilibrium distribution. In order to find this equilibrium distribution, i.e., the number of chains n_d in a particular conformation d in the equilibrium situation, we have to find the derivative of ln Q with respect to n_d. The free energy of mixing is given by $F/kT = -\ln Q$. At constant temperature and volume the variation in F is given by $dF = \sum_c \mu_c \, dn_c + \sum_{i=1}^{M}\mu_i^0 \, dn_i^0$. In equilibrium the chemical potentials $\mu_c = \mu_d = \dots \mu_{chain}$ of a chain with respect to that in bulk polymer, and $\mu_i^0 = \mu_j^0 = \dots \mu^0$ of a solvent molecule with respect to that in pure solvent are constant throughout the system. Adding one chain in conformation d (and removing r solvent molecules to maintain constant volume) changes F by an amount $(\partial F/\partial n_d)_{M,L,T,n_c \neq n_d}$, so that

$$-kT \left(\frac{\partial \ln Q}{\partial n_d} \right)_{M,L,T,n_c \neq n_d} = \mu_{chain} +$$
$$\mu^0 \sum_{i=1}^{M} \left(\frac{\partial n_i^0}{\partial n_d} \right)_{M,L,T,n_c \neq n_d} = \mu_{chain} - r\mu^0 \tag{16}$$

Roe[10] derived an analogous expression using the grand canonical partition function. In eq 16 $\mu_{chain} - r\mu^0$ is a constant at given temperature and overall composition. The derivative $\partial n_i^0/\partial n_d$ in (16) is obtained by realizing that the differentiation has to be performed at constant volume. This implies that on addition of one chain in conformation d, r solvent molecules are removed from the system, of which the spatial distribution is given by

$$r_{i,d} = -(\partial n_i^0/\partial n_d)_{M,L,T,n_c \neq n_d} \tag{17}$$

because in each layer $r_{i,d}$ solvent molecules are displaced by the $r_{i,d}$ segments that conformation d has in layer i. Obviously

$$\sum_{i=1}^{M} r_{i,d} = r \qquad (18)$$

The logarithm of the partition function is given by eq 13 and 15. The derivative of eq 13 is easily found with the help of (17), (18), and $\partial n / \partial n_d = \partial(\sum_c n_c)/\partial n_d = 1$. The result is

$$\frac{\partial \ln (\Omega/\Omega^+)}{\partial n_d} = -\ln \frac{n_d}{L} + \ln \omega_d - \ln r + r - 1 +$$
$$\sum_{i=1}^{M} r_{i,d} \ln \phi_i^0 \qquad (19)$$

For the differentiation of (15) we use also relation 17. We obtain

$$\frac{\partial(-U/kT)}{\partial n_d} = \sum_{i=1}^{M} r_{i,d} \{\chi_s \delta_{1,i} + \chi(\langle\phi_i\rangle - \langle\phi_i^0\rangle)\} \qquad (20)$$

Here χ_s is the adsorption energy parameter, defined as

$$\chi_s = -(u_s - u_s^0)/kT \qquad (21)$$

χ_s corresponds to the difference between the free energy of the transfer of a segment from bulk polymer to the surface and that of the transition of a solvent molecule from pure solvent to the surface. χ_s is positive if a segment is adsorbed preferentially to a solvent molecule. It is identical with the χ_s parameter used by Silberberg[7] and Roe.[10]

Combining eq 16, 19, and 20, we obtain

$$\ln n_d/L = \ln C + \ln \omega_d + \sum_{i=1}^{M} r_{i,d} \ln P_i \qquad (22)$$

or

$$n_d/L = C\omega_d \prod_{i=1}^{M} P_i^{r_{i,d}} \qquad (23)$$

where the constant C is given by $C = (1/r) \exp(\mu_{chain} - r\mu^0)/kT$ and the quantity P_i is defined as

$$\ln P_i = \chi_s \delta_{1,i} + \chi(\langle\phi_i\rangle - \langle\phi_i^0\rangle) + \ln \phi_i^0 \qquad (24)$$

P_i is a very important parameter determining the probability of finding a free segment (monomer) in layer i. This can be concluded from (23). For $r = 1$, this equation reads $\phi_i = n_i/L = P_i \exp(\mu - \mu^0)/kT$. As for monomers P_i is proportional to ϕ_i, we may call P_i the *free segment probability*. According to eq 24, P_i may be written as $\phi_i^0 e^{-\Delta f_i'/kT}$, where $\Delta f_i'$ is the difference in free energy (excluding the configurational entropy) between a free segment and a solvent molecule in layer i. $\Delta f_i'$ contains an adsorption energy contribution $-kT\chi_s$ for the first layer and a mixing term $kT\chi(\langle\phi_i^0\rangle - \langle\phi_i\rangle)$ arising from the segment–solvent interaction. The Boltzmann factor $\exp(-\Delta f_i'/kT)$ has to be corrected by a factor ϕ_i^0, the fraction of the volume in layer i not occupied by segments. This factor $\phi_i^0 = 1 - \phi_i$ originates from the configurational entropy term of $\ln Q$; ϕ_i represents the volume fraction which is excluded due to the presence of other segments. This effect is partly analogous to the well-known excluded volume effect for polymer chains in solution. If $\phi_i^0 \simeq 1$, this "exclusion factor" is not important. That ϕ_i^0 is an entropy contribution may also be seen by writing P_i as $\exp(-\Delta f_i/kT)$ where $\Delta f_i = \Delta f_i' - kT \ln \phi_i^0$ now also includes the configurational entropy term $k \ln \phi_i^0$.

The starting point for further analysis is eq 23. It gives the relation between the number of chains in each conformation (of which the number of segments in each layer $r_{i,d}$ is known) and the free segment probability P_i in each of the layers. Equation 23 tells us that the probability of a conformation d is proportional to the quantity

$\omega_d \prod_{i=1}^{M} P_i^{r_{i,d}}$, which we will call the *conformation probability*. From this probability, all information on the segment density distribution and other equilibrium properties (such as the train, loop, and tail size distribution) may be obtained.

Equation 23 leads immediately to the conclusion that any conformation has the same probability as its inverted conformation (in which the segments are placed in reverse order), since all $r_{i,d}$ values are the same for both conformations. Thus the inversion symmetry discussed in section II.B is an automatic result of our derivation and need not be introduced as an extra constraint, as was done by Helfand.[11] As discussed before, this is due to the fact that the partition function is maximized with respect to the number of chains in every conformation, which accounts completely for the connected nature of the chain segments.

D. Segment Density Distribution. In this section we calculate the equilibrium segment density distribution from the conformation probability $P(r)_c$, which according the the previous section can be defined as

$$P(r)_c = \omega_c \prod_{i=1}^{M} P_i^{r_{i,c}} = \omega_c \prod_{s=1}^{r} P_{k(s,c)} \qquad (25)$$

Here we have used the fact that a product of P_i over the consecutive layer numbers i may be replaced by a product over the consecutive segment ranking numbers s. In both products the free segment probabilities corresponding to each chain segment are taken once, and only the order in which the P_i's occur is different. $P_{k(s,c)}$ is the free segment probability for a segment in the layer where segment s of a chain in conformation c finds itself. This layer number is completely specified if c is given.

We define the *chain probability* as the summation of $P(r)_c$ over all possible conformations:

$$P(r) = \sum_c P(r)_c \qquad (26)$$

$P(r)$ will be needed as a normalization factor.

It is useful to consider the probability $P(s,i;r)$ that the sth segment of any chain of r segments finds itself in i. The probability $P(s,i;r)_c$ of a conformation c of which the sth segment is in i is equal to $P(r)_c$ with the additional condition that $P_{k(s,c)} = P_i$:

$$P(s,i;r)_c = \omega_c \prod_{t=1}^{s-1} P_{k(t,c)} P_i \prod_{t=s+1}^{r} P_{k(t,c)} =$$
$$\frac{\omega_c}{P_i} \prod_{t=1}^{s} P_{k(t,c)} \prod_{t=s}^{r} P_{k(t,c)} \qquad (27)$$

The last part of eq 27 is obtained by including $P_{k(s,c)} = P_i$ in both multiple products and is written in this way for later convenience. Note that $P(s,i;r)_c$ equals $P(r)_c$ if segment s in conformation c is in layer i, and zero if s is not in i. Obviously, the probability of finding the sth segment of any chain in layer i, $P(s,i;r)$, is obtained by summing over all possible conformations:

$$P(s,i;r) = \sum_c P(s,i;r)_c \qquad (28)$$

Summation of $P(s,i;r)$ over all layers gives just the chain probability $P(r)$:

$$\sum_{i=1}^{M} P(s,i;r) = \sum_c \sum_{i=1}^{M} P(s,i;r)_c = \sum_c P(r)_c = P(r) \qquad (29)$$

As mentioned above, the summation of $P(s,i;r)_c$ over all layers gives only one nonzero term $P(r)_c$.

A special case of $P(s,i;r)$ is the probability $P(r,i;r)$ that the end segment of any chain of r segments is in layer i. We use an abbreviated notation for this quantity: $P(i,r) \equiv P(r,i;r)$. We can write $P(i,r)$ as $\sum_c P(r)_c$ with the addi-

tional condition that $P_{k(r,c)} = P_i$. According to (25):

$$P(i,r) = P_i \sum_c \omega_c \prod_{s=1}^{r-1} P_{k(s,c)} \qquad (30)$$

From (29) it follows:

$$\sum_{i=1}^{M} P(i,r) = P(r) \qquad (31)$$

We designate $P(i,r)$ as the *end segment probability*.

The segment density in layer i is proportional to the summation of $P(s,i;r)$ over all the r chain segments:

$$\frac{\phi_i}{\sum_{i=1}^{M} \phi_i} = \frac{\sum_{s=1}^{r} P(s,i;r)}{\sum_{i=1}^{M} \sum_{s=1}^{r} P(s,i;r)} = \frac{1}{rP(r)} \sum_{s=1}^{r} P(s,i;r) \qquad (32)$$

Thus, if we are able to evaluate the probabilities $P(s,i;r)$ we can calculate the segment volume fraction ϕ_i in each layer. This we accomplish in two steps. First we show that $P(s,i;r)$ for any s can be expressed in the end segment probabilities $P(i,s)$ and $P(i,r-s+1)$, and next we use a well-known matrix procedure[12] to obtain the end segment probabilities $P(i,s)$.

The first step starts from eq 28 in which the summation over all the possible conformations of the entire chain, $\sum_{c(1,r)}$, is replaced by a summation over all the possible conformations of the first part of the chain, $\sum_{c(1,s)}$, and one for the second part, $\sum_{c(s,r)}$. If segment s is in layer i, the possible conformations $c(1,s)$ are independent of the conformations $c(s,r)$ because for any conformation of the first s segments all conformations for the last $r - s + 1$ segments are possible. Thus, we may use the relation $\sum_i \sum_j a_i b_j = (\sum_i a_i)(\sum_j b_j)$. Substituting (27) for $P(s,i;r)_c$ and splitting the multiple product $\omega_c = \omega_c(1,r) = \prod_{t=1}^{r-1}(\lambda_{t,t+1})_c$ in the factors $\omega_c(1,s)$ and $\omega_c(s,r)$ (compare eq 5), we may write:

$$P(s,i;r) = \sum_{c(1,s)} \sum_{c(s,r)} P(s,i;r)_c =$$
$$\frac{1}{P_i}(\sum_{c(1,s)} \omega_c(1,s) \prod_{t=1}^{s} P_{k(t,c)})(\sum_{c(s,r)} \omega_c(s,r) \prod_{t=s}^{r} P_{k(t,c)})$$

Since $P_{k(s,c)} = P_i$, the first factor between brackets equals $P(i,s)$, according to (30); the second factor is equal to $P(i,r-s+1)$ because the number of conformations of the last $r - s + 1$ segments should be equal to that of the first $r - s + 1$ segments. Therefore we have

$$P(s,i;r) = P(i,s)P(i,r-s+1)/P_i \qquad (33)$$

Thus, through eq 32 and 33 ϕ_i for r-mers can be expressed as a function of end segment probabilities of shorter chains.

The second step for the calculation of ϕ_i is to find a procedure to evaluate $P(i,s)$. If the end segment of an r-mer is in layer i, the $(r-1)$th segment can be in layer j $(1 \leq j \leq M)$, with a nonzero probability only if $j = i - 1$, $i, i + 1$. The probability $P(i,r)$ that the end segment of an r-mer is in i can then be expressed in the probabilities $P(j,r-1)$ that the end segment of an $(r-1)$-mer is in layer j. Using eq 30, we can again split the summation in two parts: $\sum_{c(1,r)} = \sum_{c(1,r-1)} \sum_{c(r-1,r)}$. As the rth segment is fixed in layer i, the summation $\sum_{c(r-1,r)}$ includes only the possible positions of the $(r-1)$th segment and may be replaced by a summation over j if $\omega_c(r-1,r)$ is replaced by λ_{j-i} and $P_{k(r-1,c)}$ by P_j. Thus

$$P(i,r) = \sum_j \lambda_{j-i} P_i P_j \sum_{c(1,r-1)} \omega_c(1,r-1) \prod_{s=1}^{r-2} P_{k(s,c)}$$

In this expression we recognize $P(j,r-1)$, so that we can write

$$P(i,r) = \sum_j \lambda_{j-i} P_i P(j,r-1) \qquad (34)$$

It may be noted here that in this derivation it was assumed that the free segment probabilities P_i for the last segment, P_j $(j = i, i \pm 1)$ for the penultimate $((r-1)$th) segment and P_k $(k = j, j \pm 1)$ for the antepenultimate segment are independent of each other. P_i, P_j, and P_k include a factor for the *average* solvent volume fractions in the layers i, j, and k. This assumption implies that backfolding of the chain (i.e., $k = i$ in the example given) is allowed under the constraint of the average excluded volume in each layer. In other words, if segment $r - 2$ is placed in i and segment $r - 1$ in $i + 1$, segment r may fold back to i with a probability P_i in which the presence of the $(r-2)$th segment is accounted for in the same way as the presence of all other segments in i. Segment $r - 2$ is, like all the previously placed segments, considered to be "smeared out" over all the lattice sites L in i. A similar approximation is made in the familiar Flory–Huggins lattice theory.[16]

Equation 34 can be expressed as a matrix multiplication by defining a vector $\mathbf{P}(r)$ with M components $P(i,r)$, whose sum according to (31) equals $P(r)$, and a matrix $\mathbf{W}$ of which the elements W_{ij} are equal to $\lambda_{j-i} P_i$. Therefore

$$\mathbf{P}(r) = \mathbf{W}\mathbf{P}(r-1) = \mathbf{W}^{r-1}\mathbf{P}(1) \qquad (35)$$

where the components of the vector $\mathbf{P}(1)$ are the "end" segment probabilities of a monomer and are thus simply equal to P_i as defined by (24). The matrix $\mathbf{W}$ is, apart from a different interpretation of P_i (in which the polymer–solvent interactions are included), identical with that used by DiMarzio and Rubin.[12]

Thus we can calculate all the end segment probabilities $P(i,s)$ for $s = 1, 2, ..., r$. Substituting (33) into (32) and realizing that $\sum_{i=1}^{M} \phi_i = nr/L$, we obtain

$$\phi_i = \frac{n}{LP(r)} \frac{1}{P_i} \sum_{s=1}^{r} P(i,s)P(i,r-s+1) \qquad (36)$$

From these M implicit equations the M ϕ_i's and the equilibrium values for P_i can be solved by an iteration procedure (see section III). We can arrange all the necessary information in the array shown in eq 37, where the

$$P = \begin{bmatrix} P(1,1) & \dots & P(1,s) & \dots & P(1,r) \\ \cdot & & \cdot & & \cdot \\ \cdot & & \cdot & & \cdot \\ P(i,1) & \dots & P(i,s) & \dots & P(i,r) \\ \cdot & & \cdot & & \cdot \\ \cdot & & \cdot & & \cdot \\ P(M,1) & \dots & P(M,s) & \dots & P(M,r) \end{bmatrix} \qquad (37)$$

components of the first column are equal to $P_1...P_i...P_M$ and the components of the sth column $P(i,s)$ are found from the first after $s - 1$ matrix multiplications. The sum of the components of the last column is equal to $P(r)$ according to (31). For the calculation of ϕ_i we need the ith row of array P, and we have to add the r products of the first and the last, the second and the penultimate, the third and the antepenultimate element, etc.

All the probabilities $P(i,s;r)$, $P(i,r)$, and $P(r)$ used in this section depend on the lattice size M and on the average segment concentration rn/ML. We shall need these quantities in a following paper where we shall discuss the case of a polymer between two plates at relatively short separation and a constant amount of polymer. For the adsorption on a single plate we relate the concentration of polymer to the bulk volume fraction ϕ_*. It appears advantageous in this case to use probabilities related to those in the bulk solution.

E. Adsorption Isotherms. In calculating adsorption isotherms and related properties, the state of a chain or a segment near the interface has to be compared to that in the bulk of the solution. Consequently, it is useful to define the probabilities of any configuration near the interface with respect to those in bulk. We shall denote bulk properties by an asterisk.

The free segment probability P_* for a segment in the bulk solution is analogously to eq 24 given by

$$\ln P_* = \chi(\phi_* - \phi_*^0) + \ln \phi_* \tag{38}$$

We now define the free segment probability p_i with respect to the bulk solution as

$$p_i = P_i/P_* \tag{39}$$

It is easily verified that p_i can be written as $(\phi_i^0/\phi_*^0) \cdot \exp(-\Delta f_i^*/kT)$, where Δf_i^* is the free energy difference (excluding the configurational entropy) for the exchange of a solvent molecule in layer i and a free segment in the bulk. The entropy factor ϕ_i^0/ϕ_*^0 accounts for the difference in the "volume exclusion" effect for a segment in layer i and a segment in bulk. It is obvious that p_* equals unity.

With eq 39 we define the vectors $\mathbf{p}(r)$ and the matrix $\mathbf{w}$ as

$$\mathbf{p}(r) = \mathbf{P}(r)/P_*^r \qquad p(i,1) = p_i \tag{40}$$

$$\mathbf{w} = \mathbf{W}/P_* \qquad w_{ij} = \lambda_{j-i}p_i \tag{41}$$

It may be noted here that the error introduced by allowing backfolding (accounting for the average volume fraction) is eliminated here to a large extent if this effect is equally important in the bulk and in layer i, because probabilities in layer i are now compared with those in bulk. Now eq 35 becomes

$$\mathbf{p}(r) = \mathbf{w}\mathbf{p}(r-1) = \mathbf{w}^{r-1}\mathbf{p}(1) \tag{42}$$

In a more explicit form, (42) can be given as shown in eq 43. Equation 36 can be written in a simpler way by re-

$$
\begin{bmatrix} p(1,r) \\ \vdots \\ p(i,r) \\ \vdots \\ p(M,r) \end{bmatrix} =
\begin{bmatrix} \lambda_0 p_1 & \lambda_1 p_1 & 0 & \cdots & \cdots & 0 \\ \lambda_1 p_2 & & & & & \vdots \\ 0 & & \lambda_1 p_i & \lambda_0 p_i & \lambda_1 p_i & \vdots \\ \vdots & & & & & 0 \\ & & & & & \lambda_1 p_{M-1} \\ 0 & \cdots & \cdots & 0 & \lambda_1 p_M & \lambda_0 p_M \end{bmatrix}^{r-1}
\begin{bmatrix} p_1 \\ \vdots \\ p_i \\ \vdots \\ p_M \end{bmatrix}
\tag{43}
$$

alizing that from (34), which remains valid if P_i and $P(i,r)$ are replaced by p_i and $p(i,r)$, follows that $p(*,r) = p(*,r-1) = p(*,1) = p_* = 1$. Equation 36 applied for bulk solution gives

$$\phi_* = nr/Lp(r) \tag{44}$$

This can be substituted in (36), giving the result

$$\phi_i = \frac{\phi_*}{r} \frac{1}{p_i} \sum_{s=1}^{r} p(i,s)p(i,r-s+1) \tag{45}$$

Also the components $p(i,s)$ can be arranged in an array p (eq 46). The sum of the components of the last vector

$$
p = \begin{bmatrix} p(1,1) & \cdots & p(1,s) & \cdots & p(1,r) \\ \vdots & & \vdots & & \vdots \\ p(i,1) & \cdots & p(i,s) & \cdots & p(i,r) \\ \vdots & & \vdots & & \vdots \\ p(M,1) & \cdots & p(M,s) & \cdots & p(M,r) \end{bmatrix}
\tag{46}
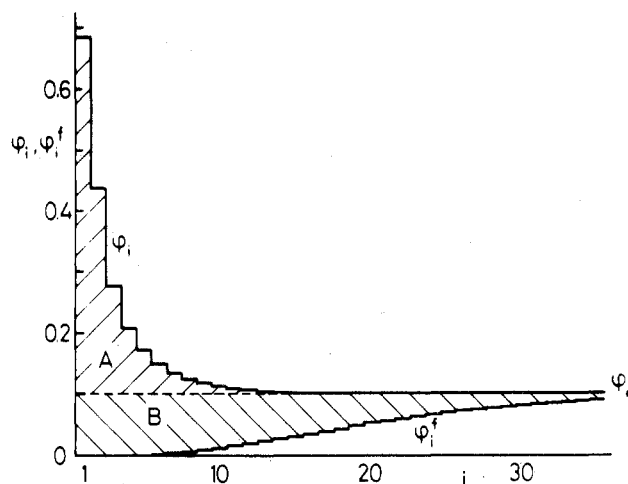$$

of p is indicated by $p(r)$, analogously to eq 31.

Figure 2. Illustration of the definition of the excess adsorbed amount Γ_{exc} and the adsorbed amount Γ. Γ_{exc} is equal to area A, while Γ equals the sum of A and B. In order to show the difference between Γ and Γ_{exc} more clearly, a rather high bulk volume fraction ($\phi_* = 0.1$) was chosen in this example. The concentration profiles have been calculated for $r = 1000$, $\chi_s = 1$, $\chi = 0.5$, and $\lambda_0 = 0.5$ (hexagonal lattice).

The simplest way of defining the adsorbed amount is to consider only the excess concentration of segments in each layer with respect to the bulk concentration. Then the excess adsorbed amount per surface site is

$$\Gamma_{exc} = \sum_{i=1}^{M} (\phi_i - \phi_*) \tag{47}$$

This definition was used by Roe. However, another definition is sometimes useful. If we want to know the number of chain segments belonging to adsorbed chains, subtracting ϕ_* from ϕ_i for all layers is not the correct procedure, since the volume fraction ϕ_i in the layers close to the surface is predominantly (or completely, for $i = 1$) due to adsorbed chains. In order to find the number of adsorbed molecules, we have to correct only for the volume fraction ϕ_i^f of free (i.e., nonadsorbed) chains that have not a single segment in the first layer (see Figure 2). In the surface layer ($i = 1$), $\phi_i^f = \phi_1^f = 0$, for the other layers $\phi_i^f \le \phi_*$, so that eq 47 gives an underestimation of the adsorbed amount. Therefore we define the adsorbed amount Γ as

$$\Gamma = \sum_{i=1}^{M} (\phi_i - \phi_i^f) \tag{48}$$

Γ thus gives the number of segments of adsorbed chains per surface site; if $\Gamma = 1$, one equivalent monolayer is adsorbed. This definition of Γ was also used by Silberberg.[7] Note that the summation of (48) contains only nonzero terms for $i \le r$.

The problem now is to find ϕ_i^f. A free chain has only one extra restriction: no segment of the chain may be in the first layer. This is equivalent to the statement that for the segments of free polymer molecules the free segment probability p_1 in the first layer equals zero (equivalent to $\chi_s = -\infty$), while in the other layers the free segment probability p_i is the same for segments of adsorbed and nonadsorbed chains. Naturally, the value of p_i for $i > 1$ is based on the total segment density ϕ_i. We may therefore define a vector $\mathbf{p}_f(1)$ with components $p_f(i,1) = (1 - \delta_{1,i})p(i,1)$ and a matrix $\mathbf{w}_f$ with elements $w_{f,ij} = (1 - \delta_{1,i})\lambda_{j-i}p_i$. The end segment probability vector for free chains is then given by

$$\mathbf{p}_f(r) = \mathbf{w}_f\mathbf{p}_f(r-1) = \mathbf{w}_f^{r-1}\mathbf{p}_f(1) \tag{49}$$

As before, we can write these vectors $\mathbf{p}_f(r)$ in an array where the sum of the components of the last vector is denoted as $p_f(r)$ (eq 50).

$$
p_f = \begin{bmatrix}
0 & 0 \ldots\ldots\ldots 0 \ldots\ldots\ldots 0 \\
p_2 & p_f(2,2)\ldots\ldots p_f(2,s)\ldots\ldots p_f(2,r) \\
\vdots & \vdots \\
p_i & p_f(i,2)\ldots\ldots p_f(i,s)\ldots\ldots p_f(i,r) \\
\vdots & \vdots \\
p_M & p(M,2)\ldots\ldots p_f(M,s)\ldots\ldots p_f(M,r)
\end{bmatrix} \quad (50)
$$

Comparing (50) with (46), we note that $p_f(i,s) = p(i,s)$ for $i > s$, $p_f(i,s) < p(i,s)$ for $2 \le i \le s$, while $p_f(1,s) = 0$. For each i, the value of $\phi_i{}^f$ can now be found from (45), substituting $p_f(i,s)$ for $p(i,s)$. For the calculation of Γ we need $\sum_{i=1}^M \phi_i{}^f$ which can be derived directly from $p_f(r)$. To that end, we realize that according to (44) $nr/L = \sum_{i=1}^M \phi_i = p(r)\phi_*$. Analogously, $\sum_{i=1}^M \phi_i{}^f = p_f(r)\phi_*$, so that (48) may be written as

$$ \Gamma = \{p(r) - p_f(r)\}\phi_* = p_a(r)\phi_* \quad (51) $$

where $p_a(r) \equiv p(r) - p_f(r)$ is the adsorbed chain probability which we shall need as a normalization constant for the adsorbed chains. It may be noted that, unlike $P(r)$ as used in the previous section, the adsorbed chain probability $p_a(r) = \Gamma/\phi_*$ is independent of M, at least for large M.

Thus, for the calculation of Γ at given ϕ_* we need the normalization constant $p(r)$, which is found by the iteration procedure to be described in section III, and $p_f(r)$. Once the iteration process has given the free segment probabilities $p_i = p(i,1)$, $p_f(r)$ and thus $p_a(r)$ are simply the result of $r - 1$ matrix multiplications according to (49).

F. Interfacial Free Energy. Using the Gibbs convention (see, e.g., ref 17), we assign to the Gibbs dividing plane a surface excess free energy F^σ, a surface excess n^σ of polymer molecules, and a surface excess $n^{0\sigma}$ of solvent molecules. The relation between these surface excesses is given by[17]

$$ F^\sigma = \gamma A + n^\sigma \mu_{\text{chain}} + n^{0\sigma}\mu^0 \quad (52) $$

where μ_{chain} and μ^0 are the chemical potentials of a polymer molecule and a solvent molecule with respect to the reference state, γ is the interfacial free energy, and A is the interfacial area. The free energy $F - F^\sigma$ of the bulk phase is then

$$ F - F^\sigma = (n - n^\sigma)\mu_{\text{chain}} + (n^0 - n^{0\sigma})\mu^0 \quad (53) $$

Combining (52) and (53), and introducing $a = A/L$ as the area per surface site, we find

$$ \frac{\gamma a}{kT} = -\frac{1}{L}\ln Q - \frac{n}{L}\frac{\mu_{\text{chain}}}{kT} - \frac{n^0}{L}\frac{\mu^0}{kT} \quad (54) $$

The term $\ln Q$ is given by eq 13 and 15. Expressions for μ_{chain} and μ^0 have been derived by Flory:[16]

$$ \mu_{\text{chain}}/kT = 1 - \phi_* - r\phi_*{}^0 + \ln \phi_* + r\chi\phi_*{}^0(1 - \phi_*) \quad (55) $$

$$ \mu^0/kT = 1 - \phi_*{}^0 - \phi_*/r + \ln \phi_*{}^0 + \chi\phi_*(1 - \phi_*{}^0) \quad (56) $$

Equation 55 can also be derived by differentiating $\ln Q$ with respect to n_c at constant T, $n_i{}^0$, and n_d ($d \ne c$); similarly, eq 56 follows from the derivative of $\ln Q$ with respect to $n_i{}^0$ at constant T, n_c, and $n_j{}^0$ ($j \ne i$).

Before substituting (55) and (56) into (54), we rewrite n_c in eq 13. With the equilibrium condition (25) and the normalization condition (26), we obtain $n_c/n = \omega_c(\prod_{i=1}^M P_i{}^{r_{i,c}})/P(r)$. Using $P(r) = P_*{}^r p(r)$ (eq 40) and eq 44, we find

$$ \frac{n_c}{L} = \frac{\omega_c \phi_*}{r}\prod_i p_i{}^{r_{i,c}} \quad (57) $$

which can be substituted into (13), giving after some rearrangement

$$ -\ln Q = n \ln \phi_* + \sum_i n_i{}^0 \ln \phi_i{}^0 + \sum_i n_i \ln p_i + U/kT \quad (58) $$

Thus the $n_c \ln n_c$ term in $\ln Q$ is replaced by a term containing the free segment probability p_i. The energy term of (58) is given by (15). Combining eq 54, 55, 56, and 58, we derive the following expression for γ:

$$
\frac{\gamma a}{kT} = \frac{\phi_1 u_s + \phi_1{}^0 u_s{}^0}{kT} + \sum_{i=1}^M \left\{ \phi_i{}^0 \ln \frac{\phi_i{}^0}{\phi_*{}^0} + \phi_i \ln p_i - (\phi_i{}^0 - \right.
$$
$$
\left. \phi_*{}^0) - (\phi_i - \phi_*)/r \right\} + \chi \sum_{i=1}^M \{\phi_i{}^0(\langle\phi_i\rangle - \phi_*) - \phi_*{}^0(\phi_i - \phi_*)\}
$$
$$ (59) $$

This equation can easily be extended for systems with more than two components. For a binary system ($\phi_i + \phi_i{}^0 = 1$) the term $-\sum_{i=1}^M \{(\phi_i{}^0 - \phi_*{}^0) + (\phi_i - \phi_*)/r\}$ reduces to $[1 - (1/r)]\Gamma_{\text{exc}}$. Apart from the $\phi_i \ln p_i$ term, all the terms of eq 59 also appear in Roe's equation (eq 36 of ref 10). In section V we give a more detailed comparison between Roe's and our theories.

III. Method of Computation

Equation 45 comprises M implicit simultaneous equations from which the M unknown $\phi_1, \phi_2, ..., \phi_M$ can be solved by an iterative procedure. If for a given ϕ_* an initial estimate for the concentration profile $\{\phi_i\}$ is used, the vector $\mathbf{p}(1)$ follows from (40) in combination with (38) and (24) and the matrix $\mathbf{w}$ from (41). In principle, a new value for $\{\phi_i\}$ could then be calculated using (45), and the procedure could be repeated by finding new values for the components $p(i,1)$, for $\mathbf{w}$ and again $\{\phi_i\}$. It turned out, however, that in this way the iteration usually does not converge. Therefore, a slightly more complicated method was applied, in which $X_i = \ln \{\phi_i/(1 - \phi_i)\}$ instead of ϕ_i was chosen as the iteration variable and Newton's method (see, e.g., ref 18) was used to improve the convergence of the iteration. This method is easier to apply if the variables are unconstrained, and therefore the variable X_i was preferred to the variable ϕ_i, which is constrained within 0 and 1.

The procedure was as follows. We indicate the initial estimate by $\{\phi_i\}^{(1)}$ and the kth solution by $\{\phi_i\}^{(k)}$. From $\{\phi_i\}^{(k)}$ the vector $\mathbf{p}(1)^{(k)}$ and the matrix $\mathbf{w}^{(k)}$ were calculated using (41). Then a new set $\{\phi_i\}^{(k')}$ was found from (45). The ($k + 1$)th solution follows from

$$ \mathbf{X}^{(k+1)} = \mathbf{X}^{(k)} - [\mathbf{G}^{(k)}]^{-1}\mathbf{g}^{(k)} $$

where $\mathbf{X}^{(k)}$ is a vector whose ith component $X_i{}^{(k)} = \ln \{\phi_i{}^{(k)}/(1 - \phi_i{}^{(k)})\}$, $\mathbf{g}^{(k)}$ is a vector with components $g_i{}^{(k)} = \ln (\phi_i{}^{(k')}/\phi_i{}^{(k)})$, and the matrix $\mathbf{G}^{(k)}$ is the Hessian,[18] with elements $G_{ij}{}^{(k)} = \partial g_i{}^{(k)}/\partial X_j$. In order to avoid the complex differentiation which is necessary to find $G_{ij}{}^{(k)}$ differences where used for the derivatives: $G_{ij}{}^{(k)} \simeq \Delta g_i{}^{(k)}/\Delta X_j$. The initial estimate $\{\phi_i\}^{(1)}$ was found from Roe's approximate expression[10] and is itself the result of a short iteration.

If we want to calculate the segment density distribution and the adsorbed amount for an r-mer, it is in principle necessary to use a lattice with more than r layers, i.e., $M > r$, since then all the possible conformations, including the completely perpendicular ones, can be taken into account. This would require a large amount of computing time and an enormous storage capacity in the computer.

TABLE I: Numerical Example of the Free Segment Probability p_i, the Polymer Volume Fraction ϕ_i, and the Volume Fraction due to Segments of Adsorbed Chains $\phi_i - \phi_i{}^f$, as a Function of the Layer Number i^a

i	p_i	ϕ_i	$\phi_i - \phi_i{}^f$	$\phi_i{}^R$
		$\chi = 0$		
1	1.6251	4.0815×10^{-1}	4.0815×10^{-1}	4.1979×10^{-1}
2	0.8343	1.7409×10^{-1}	1.7409×10^{-1}	1.8029×10^{-1}
3	0.9400	6.9353×10^{-2}	6.9342×10^{-2}	6.6164×10^{-2}
4	0.9697	3.9993×10^{-2}	3.9958×10^{-2}	2.8415×10^{-2}
5	0.9823	2.7510×10^{-2}	2.7428×10^{-2}	1.5078×10^{-2}
6	0.9888	2.1089×10^{-2}	2.0931×10^{-2}	1.0068×10^{-2}
7	0.9925	1.7388×10^{-2}	1.7117×10^{-2}	8.3540×10^{-3}
8	0.9949	1.5084×10^{-2}	1.4661×10^{-2}	8.0960×10^{-3}
9	0.9964	1.3569×10^{-2}	1.2950×10^{-2}	8.4583×10^{-3}
10	0.9974	1.2531×10^{-2}	1.1672×10^{-2}	8.9942×10^{-3}
11	0.9982	1.1798×10^{-2}	1.0656×10^{-2}	9.4711×10^{-3}
12	0.9987	1.1267×10^{-2}	9.8037×10^{-3}	9.8014×10^{-3}
13	0.9991	1.0878×10^{-2}	9.0560×10^{-3}	9.9854×10^{-3}
14	0.9994	1.0589×10^{-2}	8.3785×10^{-3}	1.0062×10^{-2}
15	0.9996	1.0374×10^{-2}	7.7506×10^{-3}	1.0076×10^{-2}
16	0.9998	1.0214×10^{-2}	7.1603×10^{-3}	1.0061×10^{-2}
17	0.9999	1.0096×10^{-2}	6.6009×10^{-3}	1.0039×10^{-2}
18	1.0000	1.0010×10^{-2}	6.0964×10^{-3}	1.0020×10^{-2}
19	1.0001	9.9499×10^{-3}	5.5645×10^{-3}	1.0007×10^{-2}
20	1.0001	9.9087×10^{-3}	5.0858×10^{-3}	1.0000×10^{-2}
		$\chi = 0.5$		
1	1.5412	6.7976×10^{-1}	6.7976×10^{-1}	6.8544×10^{-1}
2	0.8982	4.2532×10^{-1}	4.2531×10^{-1}	4.3667×10^{-1}
3	0.9843	2.5583×10^{-1}	2.5579×10^{-1}	2.4809×10^{-1}
4	0.9889	1.8157×10^{-1}	1.8146×10^{-1}	1.4778×10^{-1}
5	0.9935	1.3752×10^{-1}	1.3731×10^{-1}	9.2992×10^{-2}
6	0.9958	1.0880×10^{-1}	1.0845×10^{-1}	6.1294×10^{-2}
7	0.9972	8.8726×10^{-2}	8.8197×10^{-2}	4.2082×10^{-2}
8	0.9981	7.4009×10^{-2}	7.3261×10^{-2}	3.0050×10^{-2}
9	0.9986	6.2835×10^{-2}	6.1831×10^{-2}	2.2351×10^{-2}
10	0.9990	5.4120×10^{-2}	5.2828×10^{-2}	1.7363×10^{-2}
11	0.9992	4.7177×10^{-2}	4.5569×10^{-2}	1.4123×10^{-2}
12	0.9994	4.1550×10^{-2}	3.9603×10^{-2}	1.2034×10^{-2}
13	0.9995	3.6925×10^{-2}	3.4619×10^{-2}	1.0719×10^{-2}
14	0.9996	3.3078×10^{-2}	3.0400×10^{-2}	9.9288×10^{-3}
15	0.9997	2.9846×10^{-2}	2.6786×10^{-2}	9.4943×10^{-3}
16	0.9998	2.7109×10^{-2}	2.3662×10^{-2}	9.2974×10^{-3}
17	0.9998	2.4776×10^{-2}	2.0940×10^{-2}	9.2534×10^{-3}
18	0.9999	2.2775×10^{-2}	1.8554×10^{-2}	9.3013×10^{-3}
19	0.9999	2.1053×10^{-2}	1.6451×10^{-2}	9.3978×10^{-3}
20	0.9999	1.9565×10^{-2}	1.4592×10^{-2}	9.5133×10^{-3}

^{a} In the last column the volume fraction as calculated from Roe's theory,[10] $\phi_i{}^R$, is shown. Data are given for an athermal solvent ($\chi = 0$) and a Θ solvent ($\chi = 0.5$). Hexagonal lattice ($\lambda_0 = 0.5$), $\chi_s = 1$, $r = 1000$, $\phi* = 0.01$.

Fortunately, a faster computation with much less storage requirements is possible. With increasing i the elements $p(i,s)$, the end segment probabilities, converge to unity since far from the surface the probability of finding an end segment is equal to that in bulk. This convergence is rather slow for high s. However, it turned out that the free segment probabilities $p_i = p(i,1)$ approach unity at much smaller i (see also Table I). Therefore, the complete calculations were only carried out for the first m layers, where m is defined as the number of the last layer where p_i differs more than a predetermined value (e.g., 10^{-4}) from unity. Then all the components p_i for $i > m$ may be set equal to 1. According to eq 34:

$$p(i,s) = p_i\{\lambda_1 p(i-1,s-1) + \lambda_0 p(i,s-1) + \lambda_1 p(i+1,s-1)\} \quad (60)$$

The ith component of the sth vector follows from the $(i-1)$th, ith, and $(i+1)$th component of the $(s-1)$th vector. As $p_i = 1$ for $i > m$, all the elements in the lower left corner ($i \geq m + s$) of the array p are equal to 1 (see Figure 3).

In order to get the complete segment density distribution for the first m layers, the elements $p(i,s)$ for $i \leq m$ are required. By inspection of eq 60 it appears that the elements of groups I, IIA, and IIB (see Figure 3) are needed to calculate these elements. Thus in the computation

routine for $s \leq r/2$ the first $m + s - 1$ components of the sth vector were calculated from the first $m + s$ components of the $(s-1)$th vector, after which the elements $p(i,s-1)$ with $i > m$ were discarded by the computer and only the first m elements were stored. Similarly, for $s > r/2$ the first $m + r - s$ components of $\mathbf{p}(s)$ were calculated from the first $m + r - s + 1$ components of $\mathbf{p}(s-1)$; again only the first m components were stored.

In this way all the elements of the first m layers and thus the complete segment distribution for these layers could be calculated within a reasonable computing time, without the need of excessive storage capacity.

For the calculation of the adsorbed amount we rewrite eq 47 as $\Gamma_{exc} = \phi*(p(r) - M) = \phi*\sum_{i=1}^M \delta_{i,r}$, where $\delta_{i,r}$ is defined as $p(i,r) - 1$. The problem now is to find the sum $S(r)$ of $\delta_{i,r}$ for $i > m$: $S(r) = \sum_{i=m+1}^{m+r} \delta_{i,r}$ (see Figure 3). It can be shown that this sum can be expressed as a function of the elements of the mth and $(m+1)$th row only: $S(r) = \lambda_1 \sum_{s=1}^{r-1}\{p(m,s) - p(m+1,s)\}$. To prove this relation we realize that $\delta_{i,s} = 0$ for $i \geq m + s$, i.e., for the elements of group III in Figure 3. Next we apply (60) for $i > m$ (thus $p_i = 1$). Since $\lambda_0 + 2\lambda_1 = 1$ we have

$$\delta_{i,s} = \lambda_1\delta_{i-1,s-1} + \lambda_0\delta_{i,s-1} + \lambda_1\delta_{i+1,s-1} \quad (i > m) \quad (61)$$

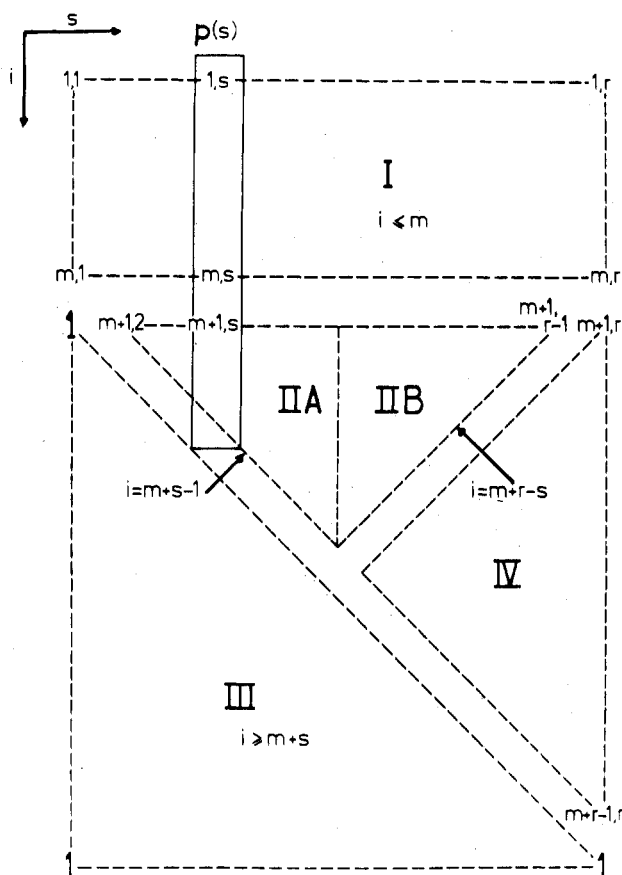Starting with $\delta_{m+1,r}$ we find $\delta_{m+1,r} = \lambda_1\delta_{m,r-1} + \lambda_0\delta_{m+1,r-1} +$

Figure 3. Schematic representation of the array *p*. In the layers beyond *m* the components p_i ($i > m$) of the first vector **p**(1) may be set equal to 1. We can distinguish four groups of elements in the array. The elements of group I ($i \leq m$) are calculated and stored in the computer memory. Those of group II ($m < i \leq m + s$ for II.A, $m < i \leq m + r - s$ for II.B) are needed for the calculation of $p(m,s)$; once $p(m,s)$ has been obtained the elements of the ($s - 1$)th vector for which $i > m$ can be discarded. All the elements of group III ($i \geq m + s$) are equal to 1. The elements of group IV ($m + r - s < i < m + s$; $r/2 < s \leq r$) are not required in the computation. The sum $p(r)$ of the components of the last vector **p**(r) is needed for the calculation of the adsorbed amount Γ. It turns out that $\sum_{i=m+1}^{m+r} p(i,r)$ can be obtained from the two sets of elements $p(m,s)$ and $p(m+1,s)$ of the *m*th and ($m + 1$)th row of the array.

$\lambda_1 \delta_{m+2,r-1} = \lambda_1(\delta_{m,r-1} - \delta_{m+1,r-1}) + (\lambda_1 + \lambda_0)\delta_{m+1,r-1} + \lambda_1 \delta_{m+2,r-1}$. Applying (61) for $\delta_{m+2,r}$ it follows that $\delta_{m+1,r} + \delta_{m+2,r} = \lambda_1(\delta_{m,r-1} - \delta_{m+1,r-1}) + \delta_{m+1,r-1} + (\lambda_1 + \lambda_0)\delta_{m+2,r-1} + \lambda_1 \delta_{m+3,r-1}$. Repeating this procedure, and using $\delta_{m+r,r-1} = 0$ we find $S(r) = \lambda_1(\delta_{m,r-1} - \delta_{m+1,r-1}) + S(r-1)$. In the same way this last sum can be expressed in the components of the (r−2)th vector, giving $S(r) = \lambda_1(\delta_{m,r-1} - \delta_{m+1,r-1} + \delta_{m,r-2} - \delta_{m+1,r-2}) + S(r-2)$. Proceeding to the left in Figure 3 we finally end up with the relation

$$S(r) = \lambda_1 \sum_{s=1}^{r-1} (\delta_{m,s} - \delta_{m+1,s}) = \lambda_1 \sum_{s=1}^{r-1} \{p(m,s) - p(m+1,s)\} \tag{62}$$

Here we made use of the fact that $S(1) = 0$.

Thus an accurate value for $p(r)$ and Γ_{exc} is found, using only the elements $p(i,s)$ for $i \leq m + 1$. The same procedure can be applied for $p_f(r)$, from which Γ is found according to eq 51.

It may be noted that this procedure of setting $p_i = 1$ for $i > m$ is not the same as a step function approach. The procedure enables us to find the sums $\sum_{i=m+1}^{r+m} \phi_i$ and $\sum_{i=m+1}^{r+m} \phi_i^f$ over the layers beyond *m* to a good approximation, although the individual ϕ_i's for $i > m$ are not calculated. This is equivalent to the evaluation of the part of the areas A and B (Figure 2) that is beyond *m*. The

accuracy of this extrapolation was shown for $r = 1000$, $\phi_* = 10^{-2}$, $\chi_s = 1$ (see also Table I). Using $m = 20$, calculated adsorbed amounts are $\Gamma = 0.91498$ and $\Gamma = 2.4455$ for $\chi = 0$ and $\chi = 0.5$, respectively. Extending *m* to 35 (the limit for $r = 1000$ on our computer) gave $\Gamma = 0.91565$ and $\Gamma = 2.4442$ for the same conditions. The differences are below 0.1% so that, in order to save computing time, in most cases $m = 20$ was chosen.

All the calculations were carried out with a DEC system-10 Model 1060 computer using a program written in Algol. The iteration procedure according to Newtons method was usually completed in five cycles with an accuracy of better than 0.01% in ϕ. The computing time increases roughly quadratic with increasing *r*. Calculations were possible for chains up to 1000 segments, in which case about 0.5 h of computation time is required.

On request the computer program will be made available by the authors.

IV. Results and Discussion

In this section we present a selection of numerical results which show the dependence of some characteristics of the adsorbed layer on parameters related to the polymer–solvent–surface system. For the latter parameters we choose the chain length *r*, the polymer–solvent interaction parameter χ, the adsorption energy parameter χ_s, and the equilibrium bulk volume fraction ϕ_*. For the adsorbed layer characteristics we take properties which in principle can be measured, as, e.g., described in the following references. Thus, we give results for the adsorbed amount[19] Γ, the fraction θ of the surface covered by segments[20] ($\theta = \phi_1$), and the fraction *p* of segments of adsorbed chains which is on the surface[21] ($p = \theta/\Gamma$). Results for another experimental variable, the layer thickness, will be discussed in another paper.

First we have to choose the type of the lattice as expressed in the fraction λ_0 of neighbors in the same layer. As has been shown by Roe,[10] theoretical results are qualitatively independent of the lattice type, while only minor quantitative differences occur. Unless otherwise stated, we confine ourselves to a close-packed hexagonal lattice: $\lambda_0 = 0.5$, $\lambda_1 = 0.25$. In a few cases a comparison will be made with a simple cubic lattice: $\lambda_0 = 2/3$, $\lambda_1 = 1/6$. More results for a cubic lattice have been published elsewhere.[22] Most of the data presented are for $\chi_s = 1$ or 3, and for two values of χ: $\chi = 0$, corresponding to an athermal solvent, and $\chi = 0.5$, equivalent to a Θ solvent. The value for ϕ_* is usually taken in the (semi-) dilute solution region, since in that region most experimental data are available; only when a comparison with other theories is desirable, we give results for composite adsorption isotherms extending over the whole range of ϕ_*. Although a more detailed comparison with other theories will not be made until the next chapter, we refer occasionally to results of other authors in the discussion of the following figures.

Table I gives a typical example of the free segment probability p_i and the concentration profile ϕ_i for $r = 1000$, $\phi_* = 10^{-2}$, $\chi_s = 1$, and $\chi = 0$ and 0.5. Also the volume fraction due to adsorbed chains, $\phi_i - \phi_i^f$, is shown. To facilitate comparison with Roe's theory, the concentration profile as calculated from his eq 29 is given. Data for $\chi = 0.5$ are plotted in Figure 4.

The dependence of p_i on ϕ_i is given in eq 24 and 39. Using the relation $\langle \phi_i \rangle + \langle \phi_i^0 \rangle = 1 - \lambda_1 \delta_{1,i}$ (see text following eq 14), we can write

$$\ln p_i = (\chi_s + \lambda_1 \chi)\delta_{1,i} + 2\chi(\langle \phi_i \rangle - \phi_*) + \ln (\phi_i^0/\phi_*^0) \tag{63}$$

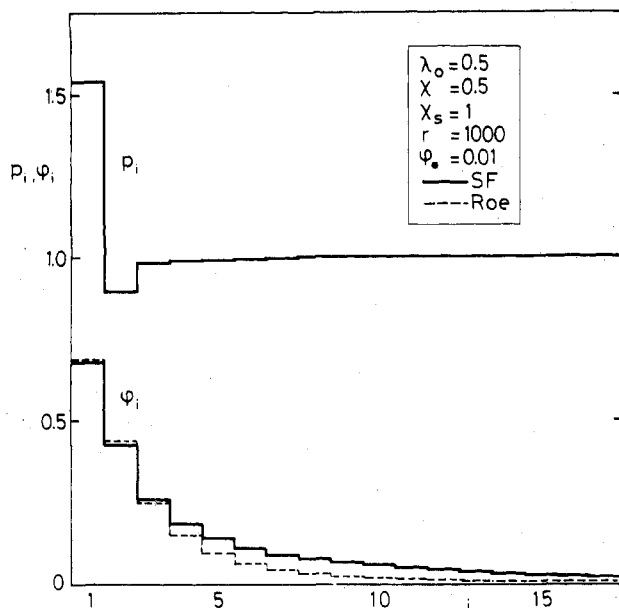In the first layer the adsorption energy dominates p_i and

Figure 4. Segment density profile ϕ_i and free segment probability p_i as a function of the distance from the surface. Hexagonal lattice (λ_0 = 0.5), χ_s = 1, χ = 0.5, r = 1000, and ϕ_* = 0.01. The dotted line is the concentration profile calculated from the theory of Roe.[10]

Figure 5. The adsorbed amount Γ (a), the surface coverage θ (b), and the bound fraction $p = \theta/\Gamma$ (c) as a function of the bulk volume fraction ϕ_*. The data apply to a hexagonal lattice (λ_0 = 0.5) and an adsorption energy parameter χ_s = 1. The chain length r is indicated. Full lines are for a Θ solvent (χ = 0.5), broken lines for an athermal solvent (χ = 0). The two dotted lines in Figure 5a apply for r = 1000 in a simple cubic lattice (λ_0 = 2/3) and χ = 0 and 0.5, respectively.

the free segment probability is higher than 1. In the other layers the factor ϕ_i^0/ϕ_*^0 is the most important one and causes p_i to be smaller than 1 and to increase with increasing i. (In other cases, e.g., at very low ϕ_*, the interaction term in (63) may be dominant, so that p_i then decreases continuously with increasing i.) A very important feature of Table I and Figure 4 is that p_i approaches unity much faster than ϕ_i approaches the bulk value ϕ_*; this is the basis for the procedure described in section III for the evaluation of the amount of adsorbed polymer present in the layers beyond i = 20. In some cases (e.g., χ = 0, i around 20 in Table I), ϕ_i is slightly lower than ϕ_* (and thus p_i slightly higher than 1), an effect which is related to the buildup of the adsorbed layer in terms of loops and tails. This will be discussed more extensively in the next paper.[23]

The segment density ϕ_i decreases continuously with increasing distance from the surface (except when ϕ_i approaches ϕ_* from below, as mentioned in the previous paragraph). In the layers close to the surface ϕ_i is slightly lower than predicted by Roe's approximate theory,[10] while further from the surface the latter theory gives a serious underestimation for the segment density. As will be shown in the next paper, the segment density at larger distances is mainly due to the presence of long dangling tails, which have been neglected in previous polymer adsorption theories.[8,24] These theories predict an exponential decay of ϕ_i with distance for homopolymers. Table I and Figure 4 show that this is approximately correct for the layers close to the surface, but not at larger distances where tails become important. The presence of tails and the concomitant occurrence of segments at relatively large distances could be very important in the application of polymers for the stabilization or destabilization of colloidal particles.

Figure 5a shows adsorption isotherms, Figure 5b the occupancy of the surface layer (θ), and Figure 5c the bound fraction $p = \theta/\Gamma$ as a function of ϕ_*. The adsorption isotherms have a Langmuir character for low values of r (for r = 1 and χ = 0, our equations reduce to the Langmuir equation), while those for high chain length are of the high affinity type often found in experiments. These features show up more clearly if the adsorbed amount Γ is plotted
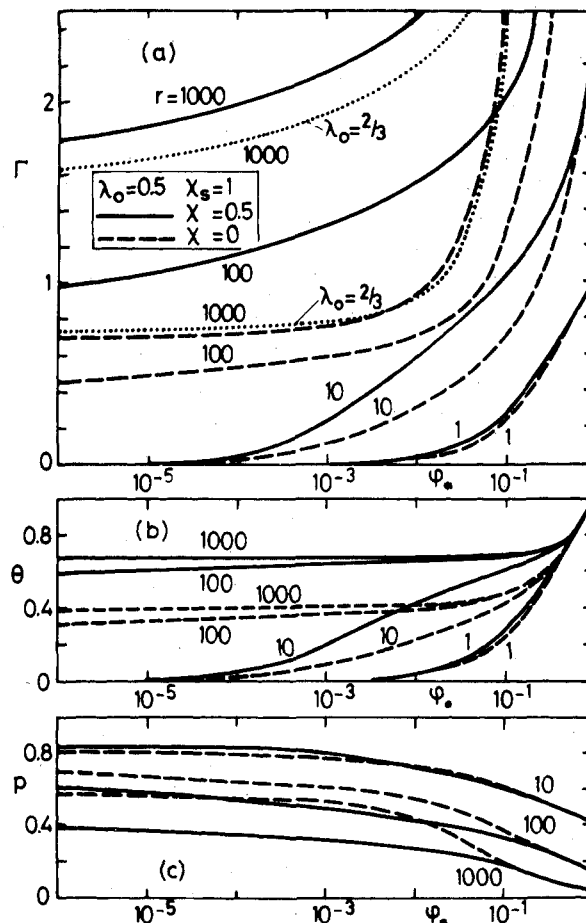
against a linear scale for ϕ_*. The overall shape of the isotherms is similar to that of the curves given by, e.g., Silberberg[7] and Hoeve[8,25] and similar trends with respect to the effects of solvent quality and molecular weight occur: the adsorption increases with decreasing solvent power and increasing chain length.

To illustrate the influence of the lattice type, two (dotted) curves for λ_0 = 2/3 (simple cubic lattice) and r = 1000 are shown in Figure 5a. The differences are small. For χ = 0.5, Γ is slighly higher for the hexagonal lattice (λ_1 = 1/4) as compared to the cubic one (λ_1 = 1/6). For χ = 0 the adsorption is slightly lower for the hexagonal lattice for low ϕ_*, but higher for high ϕ_*. The effect at χ = 0 can be explained by realizing that if λ_1 increases there are more possibilities for a segment to "cross over" to a neighboring layer, giving rise to a slightly flatter concentration profile, a lower bound fraction, and thus to a lower adsorption energy per chain. For low ϕ_* this implies a lower adsorbed amount, while for high ϕ_* there are more possibilities for loop and tail formation due to the lower volume fraction in the outer layers. For χ = 0.5, an extra effect occurs in that the "effective" adsorption energy parameter $\chi_s + \lambda_1\chi$ (see, e.g., (63)) increases with increasing λ_1; hence the adsorbed amount is higher for the hexagonal lattice.

Figure 5b demonstrates that the fraction θ of the surface which is covered by segments increases with ϕ_* for short chains but is hardly dependent on ϕ_* for higher chain lengths. As expected, θ is higher in poorer solvents, since
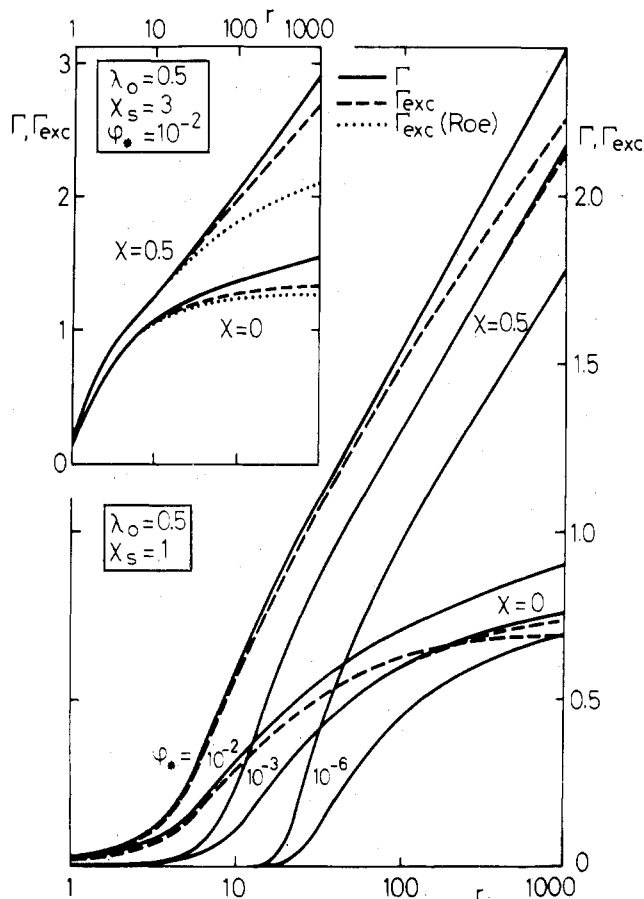
Figure 6. The adsorbed amount Γ (full lines) and the excess adsorbed amount Γ_{exc} (broken lines) as a function of the chain length r, for three values of the bulk volume fraction ϕ. and for a Θ solvent ($\chi = 0.5$) and an athermal solvent ($\chi = 0$). Hexagonal lattice, $\chi_s = 1$. The inset applies to $\chi_s = 3$ and ϕ. $= 0.01$. The dotted lines give Γ_{exc} as calculated from the theory of Roe.[10]

Figure 7. The surface coverage $\theta = \phi_1$ as a function of chain length r, for three values of the bulk volume fraction ϕ. and $\chi = 0.5$ and 0. Hexagonal lattice, $\chi_s = 1$.

the segments prefer other segments to solvent molecules as immediate neighbors. The dependence of θ on r will be discussed further in connection with Figure 7.

Figure 5c gives the dependency of the bound fraction p (i.e., the fraction of segments of adsorbed chains in contact with the surface) on the bulk volume fraction ϕ_*. The bound fraction decreases slightly with increasing ϕ_* and decreases with increasing molecular weight. Both these trends have been found experimentally.[20,21] For short chains the effect of solvent power on p is only of minor importance (for $r = 1$, $p = 1$ under all conditions), for higher chain lengths p increases with decreasing χ. This is because in good solvents the extension of the adsorbed layer is smaller than in poor solvents (at the same ϕ_*).

In Figure 6 the adsorbed amount Γ is plotted as a function of chain length at $\phi_* = 10^{-2}$, 10^{-3}, and 10^{-6}, and for $\chi = 0$ and 0.5. The dashed curves give the excess adsorbed amount Γ_{exc} (see eq 47 and Figure 2). At low ϕ_* and low r there is hardly any difference between Γ and Γ_{exc}, but as ϕ_* and r increase, Γ_{exc} becomes progressively smaller than Γ, as is to be expected. The most conspicuous feature of Figure 6 is that, at $\chi = 0$, Γ levels off at high chain lengths, while, at $\chi = 0.5$, Γ (but not Γ_{exc}) increases linearly with log r. Both Silberberg[7] and Hoeve[8,25] predict that in athermal solvents the adsorbed amount reaches a limiting value at high chain lengths, in accordance with our results. For Θ solvents, Silberberg finds again a leveling off while Hoeve predicts an increase without bounds. Although we are as yet only able to make computations up to $r = 1000$, our results seem to support Hoeve's view. However, we find for high chain lengths an important contribution of
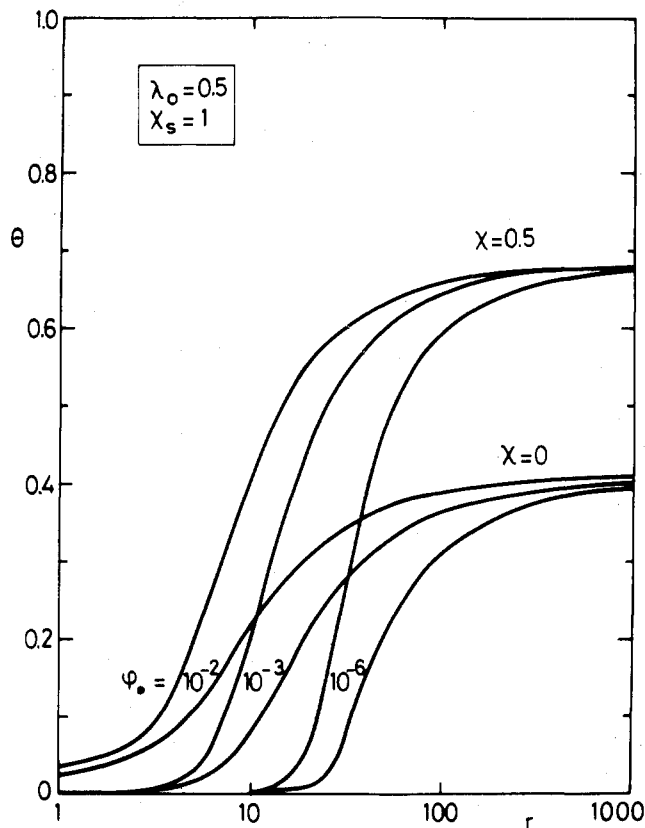
long dangling tails, and these are neglected in Hoeve's treatment.

A more quantitative comparison is possible with Roe's results.[10] This is shown in the inset of Figure 6 for $\chi_s = 3$ and $\phi_* = 10^{-2}$. Roe presents only data for Γ_{exc}. It is obvious that both for $\chi = 0$ and $\chi = 0.5$ Roe's theory underestimates Γ_{exc} at high r, the difference increasing to about 25% for $r = 1000$ (in Θ solvents) and probably much more for higher chain lengths. Thus, the sharp leveling off which Roe shows in his Figure 16 is too pronounced, and is probably due to the approximations used in his theory.

If plotted on the same scale, the curves for $\chi_s = 1$ and $\chi_s = 3$ in Figure 6 run nearly parallel. Apparently the slope of the lines depends on χ, not on χ_s. This is related to the fact that upon increase of the chain length the additionally adsorbed amount is accomodated not in trains, but in loops and tails, and is thus determined mainly by the polymer–solvent interaction.

Figure 7 shows θ as a function of chain length, at constant ϕ_*. At low r the adsorbed amount and the surface coverage are small, and there is only little effect of the solvent quality. With increasing r the surface coverage increases until a plateau is reached where θ is independent of chain length and ϕ_*. In that region, the adsorbed amount Γ still increases, but the extra segments are accomodated in layers further from the surface. The plateau of θ at high r is higher in Θ solvents, since the segments attract each other, and this attraction balances the unfavorable entropic situation at a higher θ than in good solvents.

From experiments, the surface coverage θ and the bound fraction p are often obtained not as a function of ϕ_* (see Figure 5b and 5c), but as a function of Γ. In Figure 8a and 8b the dependence of θ on Γ is given for $\chi = 0$ and $\chi = 0.5$, respectively, and in Figure 8c and 8d the corresponding
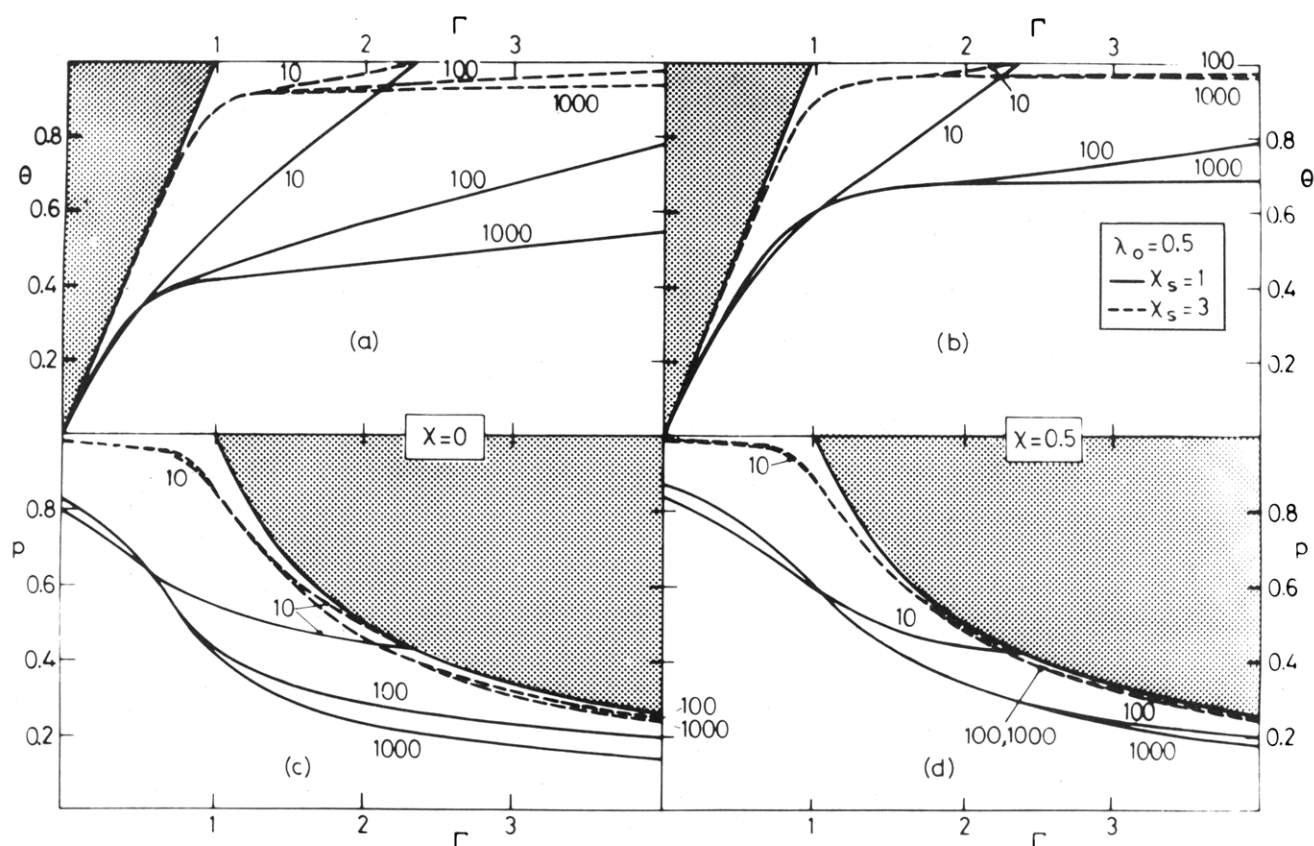
Figure 8. The surface coverage θ (a, b) and the bound fraction p (c, d) as a function of the adsorbed amount Γ, for $\chi = 0$ (a, c) and $\chi = 0.5$ (b, d). The chain length r is indicated. Hexagonal lattice, $\chi_s = 1$ (full lines) and $\chi_s = 3$ (broken lines). The shaded areas are inaccessible regions ($\theta > \Gamma$ or $\theta > 1$). Note that there exists a maximum adsorbed amount Γ^{max} (when $\phi_* = 1$) which is independent of χ or χ_s. For $r = 1$, $\Gamma^{max} = 1$; for $r = 10$, $\Gamma^{max} = 2.36$; for $r = 100$, $\Gamma^{max} = 6.25$ (not indicated in the figure); and for $r = 1000$, Γ^{max} is greater than 18.

curves for $p = \theta/\Gamma$ are shown. There are several interesting features in these graphs. For monomers, $\theta = \Gamma$ (corresponding to the straight lines in Figure 8a and 8b) and $p = 1$. The shaded areas in Figure 8 are inaccessible regions, since there θ would be higher than Γ or greater than 1. For chain molecules ($r > 1$) only part of the segments is adsorbed, and θ increases more slowly than Γ so that p decreases. As expected, the shape of the adsorbed molecules becomes less flat as the adsorbed amount increases.

At relatively low Γ the curves for different chain lengths nearly coincide. One has to realize, however, that greatly different equilibrium bulk volume fractions are involved. At high Γ (and thus high ϕ_*) the lines diverge and reach $\theta = 1$ (full surface coverage) at $\phi_* = 1$ (i.e., bulk polymer). At that point the adsorbed amount reaches its maximum value Γ^{max} which depends on r (and slightly on λ_0), but not on χ or χ_s. Clearly, Γ^{max} should lie in between 1 (completely flat chains) and r (only one end segment adsorbed). For $r = 10$, $\Gamma^{max} = 2.36$; for $r = 100$, Γ^{max} is 6.25 (not indicated in the figure) and for $r = 1000$, the maximum adsorbed amount could not yet be calculated precisely due to convergence problems of the iteration, but it is around 19. That Γ^{max} is independent of χ or χ_s is due to the fact that in bulk polymer the configuration of the chains is only determined by entropic factors, since the energy of all the segments on the surface is the same, and all segments in the other layers are in an identical environment. As is well known,[26,27] chain molecules assume unperturbed dimensions in bulk polymer.

At intermediate values for Γ, the surface coverage θ is nearly independent of Γ and r. At $\chi_s = 1$ this applies only for longer chains, but for higher adsorption energies ($\chi_s = 3$) this is true for chains as short as ten segments and up. In this region p decreases steadily with increasing Γ.

These effects are related to the accommodation of segments in the outer regions of the adsorbed layer, without altering the segment concentration in the surface layer. Again it has to be realized that for different chain lengths this region of constant θ occurs at different ϕ_*.

It can be seen from Figure 8 that θ and p increase if χ_s becomes higher. This is easily understood. Similarly, θ and p increase with increasing χ, an effect which is more pronounced at low χ_s and for high molecular weights. Naturally, the influence of the parameters χ and χ_s is strongest in the intermediate range of Γ since, for given r, all $\theta(\Gamma)$ curves converge to the same starting point (at $\Gamma = 0$) and end point (at $\Gamma = \Gamma^{max}$). It is interesting to note that *at a given adsorbed amount* the occupancy of the first layer is smaller in good solvents, so that the amount in loops and tails and the average layer thickness is greater than in poor solvents. However, in order to get the same Γ in a good solvent, much higher polymer concentrations are needed than in a poor solvent (see Figure 5a).

Koopal et al.[20] obtained experimental curves of θ and p as a function of Γ which are similar to those of Figure 8. They found that θ increases with Γ and then reaches a plateau, and is independent of molecular weight. Other experiments[21] gave also results corroborating the picture given in Figure 8.

Figure 9 shows the effect of the adsorption energy parameter χ_s on Γ (Figure 9a) and θ (Figure 9b). For infinitely long chains, adsorption occurs only if χ_s exceeds the "critical adsorption energy"[10,12] $\chi_{sc} = -\ln(1 - \lambda_1)$ which for a hexagonal lattice equals 0.288. For finite chain lengths the critical adsorption energy is smaller. With increasing χ_s the adsorbed amount and the surface coverage increase until, around $\chi_s = 3$, a semiplateau is found. The overall shape of the curves in Figure 9a strongly
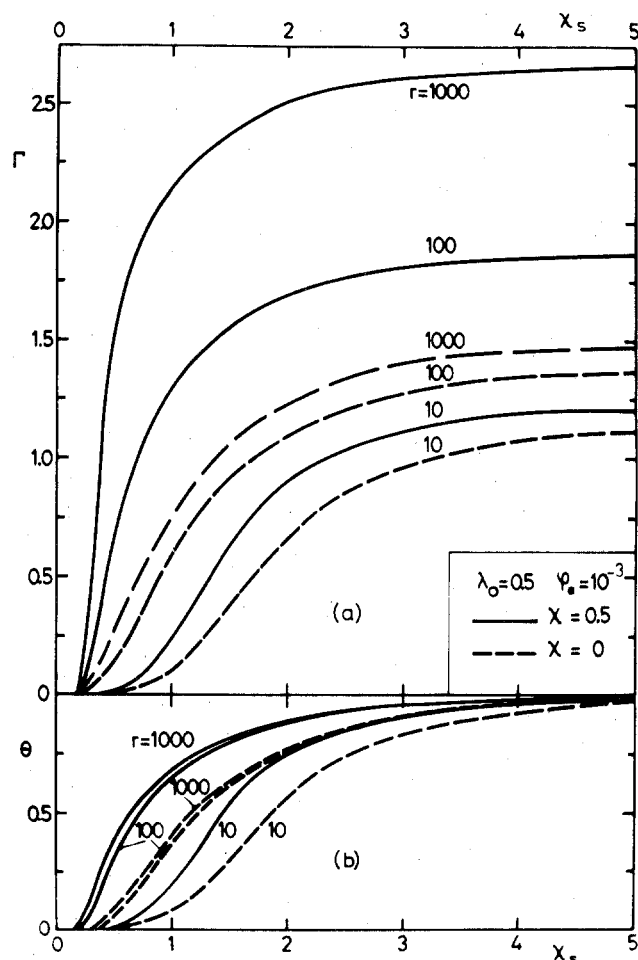
Figure 9. The adsorbed amount Γ (a) and the surface coverage θ (b) as a function of the adsorption energy parameter χ_s, for $\chi = 0.5$ (full lines) and $\chi = 0$ (broken lines). Hexagonal lattice, $\phi_* = 0.001$. The chain length r is indicated.

resembles that of Roe's Figure 15[10] (where Γ_{exc}, not Γ, is plotted), although some quantitative differences occur: at higher chain lengths the adsorbed amount is significantly higher than that according to Roe's results, and the molecular weight dependence, both for $\chi = 0$ and $\chi = 0.5$, is stronger than that predicted by Roe. As discussed above, these differences may be due to the fact that Roe's theory underestimates the contribution of tails. From Figure 9b it may be concluded that for longer chains θ is very close to unity if $\chi_s \geq 3$. The effects of solvent power and chain length on θ have been considered already in connection with Figure 7.

Other results on the structure of the adsorbed layer, such as the root-mean-square thickness of the layer, the fraction of segments present in tails and loops, and the train, tail, and loop size distribution, have been obtained. These aspects will be dealt with more extensively in a forthcoming publication.[23] At the present moment we just mention two significant results. First, the root-mean-square thickness appears to increase proportionally to the square root of the chain length. Secondly, the contribution of tails is dominant over that of the loops in the outer regions of the adsorbed layer. In dilute solutions ($\phi_* \approx 10^{-3}$) up to 15% of the segments may be present in (on average) one tail per adsorbed molecule. These effects are very important in systems where polymer is used to stabilize or destabilize colloidal suspensions.

V. Comparison with Other Theories

Many of the earlier theories[1-6] on polymer adsorption treat the case of an isolated macromolecule on a surface.

These theories are only valid for very good solvents and in systems so dilute that no measurements are possible. Their relevance for practical systems is therefore small. In these treatments the interaction between the segments is neglected, which in our terminology is equivalent to writing eq 63 simply as $\ln p_i = \chi_s \delta_{1,i}$. Indeed our model reduces completely to that of DiMarzio and Rubin[12] if we make this simplification (for a proof of this see Appendix I). All "isolated chain" theories predict that, for reasonable adsorption energies, polymers adsorb on a surface in a very flat conformation, such that the bound fraction p is close to unity. However, even if the bulk volume fraction ϕ_* is quite small the segment density in the surface region may be quite high. Therefore, the polymer–solvent interaction has to be taken into account.

The first attempts to incorporate this interaction are due to Hoeve[8,25] and Silberberg.[7] Hoeve's theory involves drastic approximations, but the general trends seem to be predicted reasonably well as shown in the previous chapter. An apparent drawback of his treatment is the neglect of tails. A quantitative comparison of his results with the present theory is difficult. Silberbergs starting point is the assumption of an "adsorbed phase" in which only segments of *adsorbed* chains are present, and the segment concentration profile is considered to be a step function. In this way no distinction between loops and tails can be made. Nevertheless his results, showing the same general trends as Hoeve's theory, are in broad agreement with ours. Also in this case a more detailed comparison is not easy.

There are two recent treatments which can be compared with the present theory in more detail. One is due to Levine et al.,[14] the other is that of Roe[10] and has already been mentioned several times.

We became aware of the theory by Levine et al. while preparing this manuscript. As discussed more extensively elsewhere[22] the basic idea of these authors is nearly the same as ours: both treatments extend DiMarzio and Rubin's[12] matrix procedure by incorporating the interaction between segments and solvent. However, Levine et al. apply their model only to the concentration profile of terminally adsorbing polymer in a cubic lattice between two plates; the authors do not attempt to use it for adsorption on a single plate or to derive the loop, train, and tail size distribution, and they do not consider a different lattice type. Apart from that there is a fundamental difference with our theory in the underlying equations. While in the present treatment the free segment probability p_i is derived from the partition function (see section II.C), Levine et al. adapt a method due to Whittington[28] to find p_i (denoted by them as the weighting factor $g(\xi)$). The result is eq 63, in which $\langle \phi_i \rangle$ is simply replaced by ϕ_i. From a physical point of view this seems to be not warranted, since a segment in layer i interacts not only with segments and solvent molecules in i but also with those in adjoining layers. In a forthcoming publication on the two plate problem we shall make a more detailed comparison with the results of Levine et al.

Roe[10] treats the adsorption of polymers in a way similar to our theory by setting up the partition function of the mixture of chains and solvent molecules near an interface. He uses the approximation that the distribution of a segment is the same for all the r segments of a chain. In the further elaboration he can then avoid the rather cumbersome matrix procedure necessary in our (and Levine's) theory. Helfand[11] has shown that Roe's treatment contains another error, because the inversion symmetry is not properly taken into account. As discussed in section II.B, Helfand corrects this by introducing a flux

TABLE II: Comparison of Numerical Results for Γ_{exc} for Oligomers ($r = 1, 2, 4$) around the Maximum in the Composite Adsorption Isotherm,[a] as Obtained from the Theories of Ash et al. (AEF),[b] Roe (R),[c] and the Present Theory (SF)

ϕ_*	$r = 1$		$r = 2$			$r = 4$		
	AEF	R/SF	AEF	R	SF	AEF	R	SF
0.1	0.64	0.6341	0.94	0.9508	0.9553	1.27	1.3123	1.3333
0.2	0.71	0.7108	0.95	0.9591	0.9681	1.28	1.3027	1.3396
0.4	0.61	0.6119	0.76	0.7587	0.7639	0.94	0.9166	0.9337

[a] Hexagonal lattice ($\lambda_0 = 0.5$), $\chi_s = 2.3$, $\chi = 0.92$.   [b] Data read from Figure 13 of ref 9.   [c] Results obtained by our own computer program.

constraint which can be expressed as the condition that the number of bonds from layer i to layer j should be equal to that in opposite direction. Since Helfand formulates this flux constraint only for infinite chain lengths, his results apply only for $r \to \infty$ and cannot be compared directly with ours.

Below, we describe in some detail the differences between the results of Roe (R),[10] Ash, Everett, and Findenegg (AEF),[9] and the present treatment (SF). The AEF theory is an extension to oligomers of the theory for monomer adsorption from regular solutions[29,30] and considers the statistical mechanics of oligomers in all possible orientations. Our theory differs from that of AEF in two respects: (1) backfolding is allowed, enabling us to use the matrix method; (2) any segment pair has a contact energy described by the χ parameter, even if two neighboring segments belong to the same molecule. The AEF theory is thus more exact than ours, but due to computational difficulties it has only been used up to $r = 4$.

For monomers ($r = 1$), our eq 45 is identical with Roe's eq 29 and to the equations given by Ono and Kondo[29] and Lane[30] for monomer adsorption from a regular solution. Our numerical results are identical with those of AEF. Roe's own calculations are slightly but consistently higher, but this is due to numerical errors, as Roe suspects already; when we programmed Roe's equations (using also here Newton's method for the iteration) we obtained identical results. This is shown in Table II. The data in this table apply to χ_s and χ values as given in Figure 13 of ref 9 ($\chi_s = 2.3$ corresponds to $\log K = 1$, $\chi = 0.92$ to $w = 0.92kT$ in AEF's terminology).

For dimers ($r = 2$), the numerical results of Roe's equations deviate slightly from ours. This is probably due to the lack of inversion symmetry in Roe's theory since the approximation that all chain segments are equally distributed should not be relevant for dimers. If this equal distribution of segments were the only assumption in Roe's treatment, his equations should reduce to ours for $r = 1$ and $r = 2$. For dimers, this is not the case.

Comparing our results for dimers and tetramers with those of AEF (see Table II), we see that there is a small difference. For dimers, this can only be caused by the overestimation of the interaction energy in our treatment, as discussed above. This effect is apparently not very important, considering that the data of Table II apply for a high value of χ. For tetramers, the backfolding effect may also play a role, and differences of the order of 5% in Γ_{exc} occur. It is possible that for high r the errors are less.

For longer chain lengths we can compare our results only with those of Roe. Figure 10 shows a few results. For short chains the differences in Γ_{exc} are very small but for longer chains the differences increase, especially in poor solvents. For $r = 1000$, $\chi = 0.5$ and in the range $\phi_* = 0$ to $\phi_* = 10^{-1}$, Γ_{exc} is about 30% higher than according to Roe. The higher adsorbed amount is mainly caused by the higher segment concentration in the outer regions of the adsorbed layer, stemming partly from loops but mainly from long
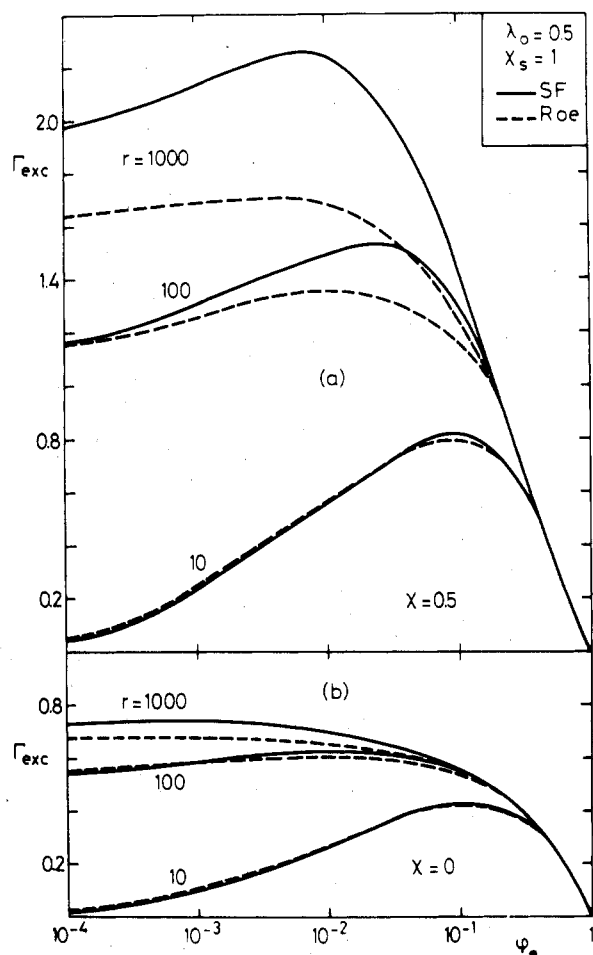

Figure 10. Comparison of composite adsorption isotherms calculated with the present theory (SF, full lines) and with the theory of Roe[10] (broken lines) for $\chi = 0.5$ (a) and $\chi = 0$ (b). Hexagonal lattice, $\chi_s = 1$. The chain length r is indicated.

dangling tails. This point will be worked out in our next paper.[23] It is in this outer region that Roe's treatment underestimates the segment density, and it is just that region which contributes most strongly to the interaction of polymer covered particles. Thus, although Roe's approximation works surprisingly well for the adsorbed amount of not too long chains, it is likely to predict far too low forces of interaction between colloidal particles in the presence of polymers. For problems in the area of colloid stability the action of relatively long tails has to be taken into account, even for adsorbed homopolymers.

We conclude with some final remarks on the dependence of the results on the type of lattice. One of the obvious drawbacks of a lattice theory is that it is not easy to relate the results to real continuous systems. One just hopes that the general trends will be described with sufficient accuracy. Fortunately these general features do not depend strongly on the lattice type chosen. This was demonstrated for a few cases in the previous section, and has been shown more extensively by Roe. In recent years there have been

a few attempts[13,15,31] to derive a continuum theory for polymer adsorption. To our knowledge, only one paper has been published[13] in which results for polymer adsorption accounting for the polymer–solvent interaction were obtained. These results are for terminally adsorbing polymers between two plates, and may be compared to the work of Levine et al.[14] (using essentially the same procedure as ours). It turns out that the calculated concentration profiles and the effect of the interaction on them are very similar, the differences being of the same order of magnitude as what is typical when different lattices are used. Thus, it seems that the continuum and lattice theories give, generally speaking, similar results. In a future paper on the interaction of two plates in the presence of polymer, we shall discuss these points in more detail.

Appendix I

Relation between Our Procedure and the Model of DiMarzio and Rubin. In our terminology, the combination of eq 2.5 and 2.11 of the paper of DiMarzio and Rubin[12] can be written as

$$v_i(r) = \frac{1}{rp(r)}\{p_i \mathbf{u}^T \mathbf{p}_i(r-1) + \sum_{s=1}^{r-1} \mathbf{u}^T \mathbf{p}_i(s-1)p(i,r-s+1)\}$$

(A.1)

Here $\mathbf{u}^T$ is the row vector $(1, 1, ..., 1)$ and $\mathbf{p}_i(s) = \mathbf{w}^s \Delta_i$, with Δ_i a column vector with the ith component equal to 1 and all the other components zero. According to our notation, the symbols $N + 1$ and θ_i of DiMarzio and Rubin have to be replaced by r and $\ln p_i = \chi_s \delta_{1,i}$, respectively. Equation A.1 can be simplified by writing the matrix $\mathbf{w}$ as a product of two symmetrical matrices $\mathbf{x}$ and $\mathbf{y}$, of which the elements are $x_{ij} = p_i \delta_{i,j}$ (only nonzero elements along the diagonal) and $y_{ij} = \lambda_{j-i}$. Then $\mathbf{w} = \mathbf{xy}$ and the transpose of $\mathbf{w}$ equals $\mathbf{w}^T = \mathbf{yx}$. Using elementary matrix algebra

$$\mathbf{u}^T \mathbf{p}_i(s-1) = \mathbf{u}^T \mathbf{w}^{s-1} \Delta_i = (\mathbf{u}^T \mathbf{w}^{s-1} \Delta_i)^T = \Delta_i^T (\mathbf{yx})^{s-1} \mathbf{u} =$$
$$\Delta_i^T (\mathbf{x}/p_i)(\mathbf{yx})^{s-1} \mathbf{u} = p_i^{-1} \Delta_i^T (\mathbf{xy})^{s-1} \mathbf{xu} =$$
$$p_i^{-1} \Delta_i^T \mathbf{w}^{s-1} \mathbf{p}(1) = p(i,s)/p_i$$

Thus eq A.1 can be written much more simply as

$$v_i(r) = \frac{1}{rp(r)} \sum_{s=1}^{r} p(i,s)p(i,r-s+1)/p_i$$

(A.2)

Since $v_i = n_i/\sum_i n_i = L\phi_i/nr$ this equation is identical with our eq 44 and 45 combined.

Appendix II

List of Symbols. In the following list the most important or most frequently used symbols have been collected.

A	area
a	A/L, area per lattice site
$c, d, ...$	specification number for chain conformation
F, F^σ	free energy of the system with respect to the reference state, surface excess free energy
$i, j, ...$	layer number
k	Boltzmann's constant
$k(s,c)$	number of the layer in which the sth segment of a chain in conformation c finds itself
L	number of lattice sites per layer
M	number of lattice layers
m	number of layers for which complete calculations have been performed
n, n^0	number of polymer molecules, number of sol-

	vent molecules, in the system
n_c	number of polymer molecules in conformation c
n_i, n_i^0	number of polymer segments, number of solvent molecules, in layer i
$n^\sigma, n^{0\sigma}$	surface excess of polymer molecules, surface excess of solvent molecules
P_i, P_*,	free segment probability in layer i, in bulk
$P_{k(s,c)}$	solution, and in the layer where the sth segment of a chain in conformation c is present (eq 24)
$P(i,s)$	end segment probability, i.e., the probability that the end segment of an s-mer is in layer i
$\mathbf{P}(s)$	column vector with M components $P(i,s)$
$P(r)$	chain probability, i.e., sum of the components of $\mathbf{P}(r)$ (eq 26 and 31)
$\mathbf{P}$	array of all the r vectors $\mathbf{P}(s)$
$P(r)_c$	conformation probability (eq 25)
$P(s,i;r)$	probability that the sth segment of an r-mer is in layer i
$P(s,i;r)_c$	probability of conformation c of an r-mer of which the sth segment is in i
p	bound fraction θ/Γ
p_i	P_i/P_*, free segment probability in layer i with respect to the bulk solution
$p(i,s)$	$P(i,s)/P_*^s$, end segment probability of an s-mer with respect to the bulk solution
$\mathbf{p}(s)$	column vector with M components $p(i,s)$
$p(r)$	chain probability with respect to the bulk solution, i.e., sum of the components of $\mathbf{p}(r)$
$\mathbf{p}$	array of all the r vectors $\mathbf{p}(s)$
$p(s,i;r)$	probability (with respect to bulk solution) that the sth segment of an r-mer is in i
$p_f(i,s)$	end segment probability (with respect to bulk) for free, nonadsorbed s-mers
$\mathbf{p}_f(s)$	column vector with M components $p_f(i,s)$
$p_f(r)$	chain probability (with respect to bulk) of free chains, i.e., sum of the components of $\mathbf{p}_f(r)$
$\mathbf{p}_f$	array of all the r vectors $\mathbf{p}_f(r)$
$p_a(r)$	$p(r) - p_f(r)$, chain probability (with respect to bulk) of adsorbed chains
$Q(M, L, T, \{n_c\})$	partition function at given distribution of conformations
r	number of segments per chain
$r_{i,c}$	number of segments that a chain in conformation c has in layer i
$s, t, ...$	segment ranking number
T	absolute temperature
U	energy of the system with respect to the reference state
u_s, u_s^0	adsorption energy of a segment, and of a solvent molecule
W	matrix with elements $W_{ij} = \lambda_{j-i} P_i$
w	matrix with elements $w_{ij} = \lambda_{j-i} p_i$
w_f	matrix with elements $w_{f,ij} = \lambda_{j-i} p_i(1 - \delta_{1,i})$
z	coordination number of the lattice
Γ, Γ_{exc}	adsorbed amount, and excess adsorbed amount (eq 47 and 48)
γ	surface tension
$\delta_{i,j}$	Kronecker delta; if $i = j$, $\delta_{i,j} = 1$; if $i \neq j$, $\delta_{i,j} = 0$
λ_{j-i}	fraction of nearest neighbors in layer j around a site in i; $\lambda_{j-i} = 0$ if $|j - i| \geq 2$
λ_0, λ_1	fraction of nearest neighbors in the same layer, and in an adjacent layer
$(\lambda_{s,s+1})_c$	fraction of nearest neighbors that a site in the layer, where the sth segment of conformation

c is found, has in the layer where the $(s + 1)$th segment is; thus $(\lambda_{s,s+1})_c$ equals λ_0 if s and $s + 1$ are in the same layer, and λ_1 if s and $s + 1$ are in adjacent layers

θ ϕ_1, surface coverage or segment volume fraction in the first layer

μ_{chain}, μ^0 chemical potential of a chain, and a solvent molecule with respect to the reference state

ν_i number of previously occupied sites in layer i (eq 9)

ϕ_i, ϕ_* segment volume fraction in layer i, and in the bulk solution

ϕ_i^f volume fraction due to nonadsorbed chains

ϕ_i^0, ϕ_*^0 solvent volume fraction in layer i, and in the bulk solution

$\langle \phi_i \rangle, \langle \phi_i^0 \rangle$ site volume fraction of segments, and solvent, in layer i (defined in eq 14)

χ Flory–Huggins polymer–solvent interaction parameter

χ_s differential adsorption energy parameter (eq 21)

Ω, Ω^+ combinatory factor for the mixture of polymer and solvent, and for amorphous bulk polymer

$\omega, \omega(n)$ number of ways of placing the first chain, and the first n chains, in an empty lattice (eq 9 and 10)

ω_c ratio between the number of arrangements of a chain in conformation c and that of a chain in bulk polymer (eq 5)

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