

## Bridging interactions in dilute solutions of adsorbing polymers

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## ABSTRACT

A simple formalism is suggested, to calculate the most likely configuration of a finite polymer, between two surfaces on which the monomers can adsorb. It is shown that at large adsorption energies for monomers on surfaces, the polymer is mostly collapsed on one surface and very few bridges between surfaces are created, therefore the bridging interaction is weak. On the other hand, at very low adsorption energies, although there are more bridges formed, the long-range interactions between surfaces are also weak. The optimal adsorption energy, at which the long-range attractive force between surfaces has a maximum, is calculated as a function of separation distance between surfaces, for a solution of dilute adsorption polymers, using the assumptions that the monomer-monomer and monomer-solvent interactions can be neglected.

**Keywords:** *polymer brushes, adsorbing polymers, bridging interactions, random walk, first return.*

## 1. INTRODUCTION

Grafted polymer brushes have been often used to stabilize colloidal dispersions, because of the steric repulsion that develops when two brushes are overlapping [1]. However, if the monomers are adsorbed on the surfaces, the opposite effect might also occur – because a polymer “bridge” may reach the other surface and therefore generates attraction [2]. This “bridging” interaction has been already used to induce flocculation of colloidal particles in water purification systems [3], and might also play a role in various biological processes, such as the attachment of biological cells on foreign surfaces. Because bridging requires interdigitation of brushes, it is more difficult to understand it in terms of simple theoretical models, than the steric interaction.

The lattice model of Scheutgens and Fleer [4] for the adsorption of a polymer molecule on a single plate have been extended to the attractive interaction between plates by Li and Ruckenstein [5]. The self-consistent field theory (for adsorption on one plate) of Varoqui [6] has been used to calculate the bridging interactions between two plates by Podgornik [7], and was extended to polyelectrolytes by Borukhov et al. [8] Additional van der Waals interactions have been accounted for, in this framework, by Huang and Ruckenstein [9]. Whereas these self-consistent field theories can provide a general description of the system (e.g. the monomer distribution in overlapping brushes or the forces between plates), they cannot provide microscopic information (such as the number of bridges formed, and their dependence on the monomer-surface interaction).

The approximation of a polymer confined between walls as a random walk on a lattice is usually treated in a matrix formalism suggested by DiMarzio and Rubin [10], which allows

one to calculate the fraction of loops, bridges and trains, and consequently the polymer-mediated interaction between plates as functions of the separation between plates and the adsorption energy. It was later shown [11] that the interaction between plates depends critically on the value of the adsorption energy,  $\theta_c = \frac{A}{kT}$ ,

with  $A$  being the adsorption energy of a Kuhn segment on the surface,  $k$  the Boltzmann constant and  $T$  the absolute temperature. If  $\theta < \theta_c$ , the interaction between plates was shown to be repulsive (because of the repulsion generated by the entropic confinement of the polymer), at  $\theta = \theta_c$  there is no interaction, whereas for  $\theta > \theta_c$  the attraction increases monotonically with decreasing plate separation (the formalism does not take into account the steric repulsion due to monomer volume exclusion effect). When  $\theta$  is large, the attraction is actually decreased, because the polymer collapses on one surface and less bridges are formed. The purpose of this paper is to suggest an alternative approach, in which the partition function of the system is approximated by the most likely configuration via a minimization procedure, which was employed recently for the adsorption of a polymer on a single surface.<sup>12</sup> The dilute polymer is approximated by an 1D non-interacting random walk starting on one surface, for which the probabilities of reaching the other surface or returning to the initial surface can be obtained as functions of the number of steps (the size of the bridges and loops, respectively). It is shown that the optimal adsorption energy for Kuhn segments (which maximize the attraction between plates) depends on the plate separation, and can be easily calculated.

## 2. THEORETICAL MODEL

The polymer is considered composed of Kuhn segments, that can have orientations independent of each other, and the segment distribution for non-interacting segments is provided by a random walk. Furthermore, any configuration of a polymer can be

described by a combination of a number of  $nl_i$  loops (random walks that returns to the same surface from which they departed after “ $i$ ” steps),  $nb_i$  bridges (random walks that reach the opposite surface after “ $i$ ” steps) and one tail (a random walk that ends up

without reaching any surface). The partition function of such a polymer is therefore given by:

$$Z = \sum_{j=1}^N \exp\left(-\frac{U_j}{kT}\right) = \sum_{[nl_i, nb_i]} \exp\left(-\frac{U_{[nl_i, nb_i]}}{kT}\right) \quad (1)$$

where the sum over “ $j$ ”, that runs over all the  $N$  Kuhn segments is replaced by a sum over all possible configurations of  $nl_i$  loops,  $nb_i$  bridges and one tail, compatible with a polymer composed of  $N$  Kuhn lengths.

The energy  $U$  associated with the configuration energy should account for the interactions between monomers and surfaces, monomers and monomers and monomers and solvent. A mean field approximation, in which a minimum energy is associated with each individual loops, tails and bridges was proposed recently [12,13]. However, if the solvent is neutral and the polymer solution dilute, the largest contribution to the energy comes from the interactions between monomers and surfaces, which can be calculated exactly:

$$U_{[nl_i, nb_i]} = -A \sum_i (nl_i + nb_i + 1) = -A(n_s + 1) \quad (2)$$

where one considers that the interaction energy between segments and surface is equal to  $-A$  if the segment is adsorbed on the surface and zero otherwise, the sum is over the number of loops and bridges that contain “ $i$ ” segments, and  $n_s$  is the total number of loops and bridges.

The probability for a “loop” or a “bridge” to occur in a configuration, when there are two parallel surfaces at a distance of  $D$  Kuhn segments (where  $D$  is an integer) and the interaction energy  $U=0$ , is provided by the probability that a random walker, that departs from a surface, will return to the same surface or reach the opposite one after “ $i$ ” steps, without having reached any of the two surfaces before. A random walker starting at a surface makes the first step away from the surface, and then either returns to the initial surface after  $2, 4, 6, \dots$  steps or reaches the other surface after  $D, D+2, D+4$  steps, where the number of steps should be smaller than the length  $N$  of the polymer (a random walk that after  $N$  steps does not reach any surface is a “tail”).

The probabilities of the “first return” to the origin after “ $i$ ” steps of a random walk, that start at a distance of  $c$  steps from the origin have been calculated by Chandrasekhar for both a reflecting and an absorbing wall [14]. The presence of the second surface at a distance  $D$  (on which the walker can be also adsorbed) complicates the problem, although it was shown long ago by Huygens that the probability of reaching either wall (regardless of the number of steps) is inverse proportional to the distance to the wall (the “gambler’s ruin” problem) [15]. The probability of reaching for the first time a surface at a distance  $D$ , without having reached the surface at  $0$ , can be calculated as follows [15].

Assuming that the probability of a step forward is equal to the probability of a step backward, the probability to reach a point at a distance  $c$  after  $i+1$  steps is provided by :

$$p_{i+1}(c) = \frac{1}{2} p_i(c-1) + \frac{1}{2} p_i(c+1) \quad (3)$$

By multiplying with a variable  $z^{i+1}$  and summing over “ $i$ ”, one obtains:

$$\sum_{i=0}^{\infty} p_i(c) z^i = G(z, c) = \frac{z}{2} G(z, c+1) + \frac{z}{2} G(z, c-1) \quad (4)$$

When “ $c$ ” represents the starting point of the walk, the generating function  $G$  of the probabilities to reach the surface at  $D$  in “ $i$ ” steps for the first time, without returning to the origin, obeys the boundary conditions:

$$G(z, D) = 1 \quad (5a)$$

$$G(z, 0) = 0 \quad (5b)$$

which simply state that a walker starting at  $D$  always reaches first the surface at  $D$  and never reaches first the surface at  $0$ . The solution of Eq.(4) subject to the boundary conditions (5) is unique, and provided by:<sup>13</sup>

$$\sum_{i=0}^{\infty} p_i(c) z^i = z^{D-c} \frac{(1+\sqrt{1-z^2})^c - (1-\sqrt{1-z^2})^c}{(1+\sqrt{1-z^2})^D - (1-\sqrt{1-z^2})^D} \quad (6)$$

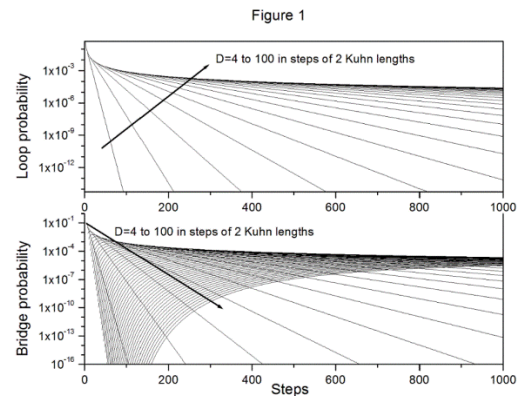
The probability that a random walker starting from a surface to reach the other surface after “ $i$ ” steps, hence to form a bridge (since the first step is always away from the surface), is therefore given by:

$$\sum_{i=1}^{\infty} p b_i z^i = z^{D-1} \frac{(1+\sqrt{1-z^2}) - (1-\sqrt{1-z^2})}{(1+\sqrt{1-z^2})^D - (1-\sqrt{1-z^2})^D} \quad (7a)$$

and the probability of first return to the origin, hence forming a loop, by:

$$\sum_{i=1}^{\infty} p l_i z^i = z \frac{(1+\sqrt{1-z^2})^{D-1} - (1-\sqrt{1-z^2})^{D-1}}{(1+\sqrt{1-z^2})^D - (1-\sqrt{1-z^2})^D} \quad (7b)$$

where  $D$  represents the minimum number of steps required to reach the opposite surface (the distance between surfaces, measured in Kuhn lengths). These probabilities can be calculated as usual, by expanding in series the generating functions from Eqs. (7a and 7b) and identifying the terms of  $z$  powers. In Figure 1, the probabilities to return to the initial surface or to reach the other surface are plotted for the first 1000 steps, for a separation  $D$  between plates of 100 Kuhn lengths.



**Figure 1.** Probabilities of first return to the surface (loops) / first reaching the other surface (bridges) after “ $i$ ” steps, for a non-interacting random walk, for various separation distances  $D$  between surfaces, between 4 and 100 Kuhn lengths (in steps of 2 Kuhn lengths).

The partition function becomes:

$$Z = \sum_j \exp\left(-\frac{U_j}{kT}\right) = \sum_{n_1, n_b, n_t} \frac{n_s!}{n_1! n_b! n_t!} p_l^{n_1} p_b^{n_b} \dots \exp\left(\frac{A}{kT} (n_s + 1)\right) \quad (8)$$

subject to the constraint that the sum of the segments in the loops, bridges and in the tail to be equal the total number  $N$  of the Kuhn segments of the polymer:

$$\sum_i (inl_i + inb_i) = N \quad (9)$$

where the values  $i < N$  belong to a loop or bridge and the values  $i > N$  to a tail (walks that need more than  $N$  steps to reach a surface).

The equations for the most likely configuration are provided by the derivative of the logarithm of the partition function Eq.(6) subject to the constrain (7), with respect to all  $n_l$  and  $n_b$ :

$$\frac{d}{dn_l} \left( \ln \left( \frac{n_s!}{n_1! n_b! n_t!} p_l^{n_1} p_b^{n_b} \dots \exp\left(\frac{A(n_s + 1)}{kT}\right) \right) - \lambda \left( N - \sum_i (inl_i + inb_i) \right) \right) = 0 \quad (10a)$$

$$\frac{d}{dn_b} \left( \ln \left( \frac{n_s!}{n_1! n_b! n_t!} p_l^{n_1} p_b^{n_b} \dots \exp\left(\frac{A(n_s + 1)}{kT}\right) \right) - \lambda \left( N - \sum_i (inl_i + inb_i) \right) \right) = 0 \quad (10b)$$

After employing the Sterling approximation,  $\ln(n!) = n \ln(n) - n$ , Eqs.(10) become :

$$n_l = n_s \left( p_l \exp\left(\frac{A}{kT} - i\lambda\right) \right) \quad (11a)$$

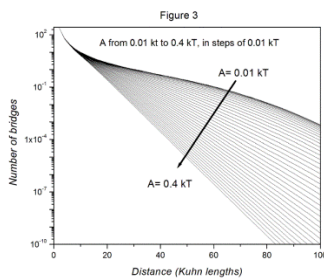
$$n_b = n_s \left( p_b \exp\left(\frac{A}{kT} - i\lambda\right) \right) \quad (11b)$$

where  $\lambda$  is a Lagrange multiplier, which can be obtained from the condition that the sum over all possible  $i$  values to be equal to  $n_s$ :

$$\sum_i (n_l + n_b) = \sum_i n_s (p_l + p_b) \exp\left(\frac{A}{kT} - i\lambda\right) \quad (12)$$

### 3. RESULTS AND DISCUSSION

The number of bridges for a polymer with  $N=1000$  is plotted vs. the separation distance between surfaces in Figure 3, for various values of  $A$ . One can see that the number of bridges decreases drastically with increasing adsorption, because a larger adsorption increases the number of short loops (the polymer being almost completely adsorbed on one surface). This implies that the attractive force between surfaces does not vary monotonically with  $A$ : for  $A=0$  (no adsorption energy), the attractive force vanishes. The attraction force is also negligible for strong adsorption interactions, because in this case the adsorbing polymer collapses on one surface, and does not reach the other one.



**Figure 3.** Number of bridges formed by one polymer of length  $N=1000$  Kuhn segments, as a function of the distance between surfaces, and various adsorption energies (between  $0.01 kT$  and  $0.4 kT$ , in steps of  $0.01$

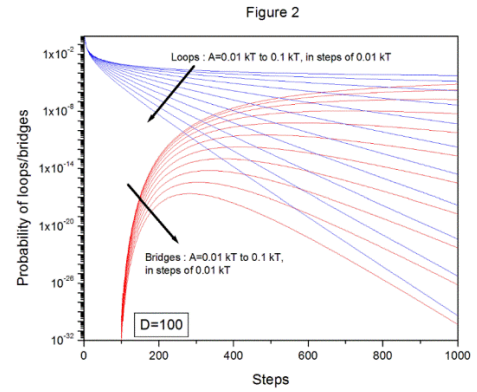
which, because  $n_s = \sum_i (n_l + n_b)$ , reduces to:

$$\sum_i \left( p_l \exp\left(\frac{A}{kT} - i\lambda\right) + p_b \exp\left(\frac{A}{kT} - i\lambda\right) \right) = 1 \quad (13)$$

which can provide  $\lambda$ . Once  $\lambda$  is known,  $n_s$  can be determined from the constrain Eq.(9).

The terms  $p_l \exp\left(\frac{A}{kT} - i\lambda\right)$  and  $p_b \exp\left(\frac{A}{kT} - i\lambda\right)$  represent

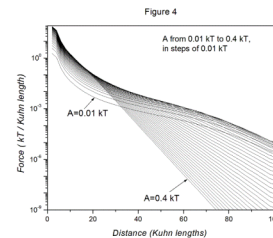
the new probabilities of loops and bridges formation, in the presence of short-range (adsorption) interactions between monomers and the surface. They are plotted in Figure 2, for  $D=100$ , and various adsorption energies  $-A$ .



**Figure 2.** Probabilities of loop/ bridge formation after “ $i$ ” steps, for a separation distance of  $D=100$  Kuhn lengths between surfaces, and various adsorption energies for monomers on surfaces, between  $0.01 kT$  and  $0.1 kT$  (in steps of  $0.01 kT$ ).

$kT$ ). At  $D=100$ , the number of bridges formed decreases with  $A$  by about 10 orders of magnitude.

The attractive force between plates (calculated as the derivative with respect to the distance between the plates of the total energy of the most likely polymer configuration, measured in units of  $kT$  divided by the Kuhn length, is plotted in Figure 4 as a function of distance, for various  $A$  values. At large separations, the force is large for low  $A$  values (because of a drastic decrease in the number of bridges with increasing  $A$ ), while at low separations the force is in general larger for larger  $A$  values.

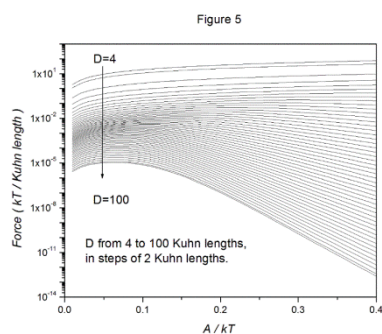


**Figure 4.** Attractive forces between surfaces (arbitrary units), as a function of the distance between surfaces, for various  $A$  values. At large separations, large  $A$  values correspond to lower forces, but at small separations smaller  $A$  values provides also lower forces.

In the extreme case, when the separation between the surfaces is only 2 Kuhn segments, the probability of a loop or a

bridge formation become equal, and independent of  $A$ . At this distance, the attraction increases monotonically with  $A$ .

In general, for larger distances, the force as a function of  $A$  exhibits a maximum which depends on the distance between surfaces, as shown in Figure 5.



**Figure 5.** Attractive forces between surfaces as functions of  $A$  (and various distances  $D$ ) shows that an optimal value of  $A$  exists for each separation distance.

The value of that maximum, as a function of distance, is represented in Figure 6. This maximum shows that the long-range

#### 4. CONCLUSIONS

Polymers that adsorb on colloidal particle surfaces can create bridges between adjacent particles, and generate long range attractions between them, leading to their flocculation. However, if the attractive short-range adsorption energy for monomers on a surface is too strong, the polymer collapses on one surface, and create very few bridges between surfaces; if it is too weak, then the long-range attractive forces between colloidal surfaces are also weak. A formalism to calculate the bridging interactions between particles immersed in a dilute solution of polymers of finite length

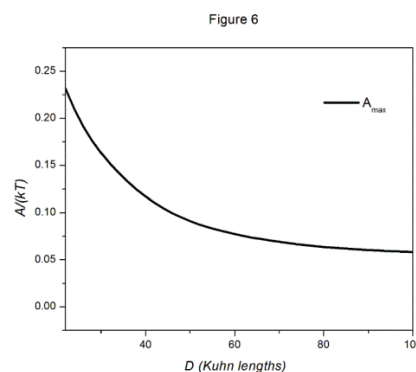
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attractive force between surfaces, due to dilute polymers, can be tailored by changing the nature of the polymer (e.g., the adsorption energy of monomers on surfaces), in such a manner that the flocculation of colloidal suspensions becomes optimal. A too weak adsorption energy, as well as a too strong adsorption energy, do not generate a significant bridging force.



**Figure 6.** Adsorption energy that provides the maximum force, as a function of the distance at which this force is measured. The strongest long-range bridging attraction (at  $D = 100$ ) requires a value of  $A$  of about  $0.06 kT$ .

was suggested, based on the calculation of the most likely polymer configuration. It was shown that the long-range attractive forces between colloidal particles exhibit a maximum, as a function of the adsorption energy between monomers and the surface, which depends on the separation between adjacent particles. The optimal adsorption energy, which maximizes the bridging force at various separation distances, was calculated for a dilute solution of adsorbing polymers, for which the monomer-monomer and monomer-solvent interactions can be neglected.

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