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To cite this version:


HAL Id: jpa-00247975
https://hal.archives-ouvertes.fr/jpa-00247975
Submitted on 1 Jan 1994
Confined chains with specific interactions, bridges, loops and osmosis

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(Received 28 June 1993, revised 5 November 1993, accepted 23 November 1993)

Abstract. — We describe the macroscopic behavior of Gaussian chains confined between impenetrable surfaces and having ends interacting with the surfaces taking into account all multiple reflections from the two surfaces. The statistics of chains with the absorbing boundary conditions are used and proper interactions between the chain ends and the surfaces are included. We determine and study the forces in terms of the characteristics of the surface interactions and the ratio $d/S$ of the distance of the surfaces to the mean radius of gyration of the chain. Suitable choices of the parameters of the model reproduce many features observed experimentally for homopolymers and block copolymers.

I. Introduction.

Recently the study of chains in between impenetrable surfaces found increased interest because of its applications in many fields [1]. The control of the stability of colloidal dispersions by means of polymers which can exert repulsive or attractive forces is one while adhesion, lubrication and mechanical integrity of different polymeric species are some others. Recent techniques capable to measure directly forces between plane surfaces bearing polymers made possible well controlled experiments on model systems and the determination of the dependence of the macroscopic properties on molecular parameters. Delicate experiments on homopolymers and block copolymers have been performed where repulsive but also simultaneous attractive and repulsive forces have been detected [2-5]. All these make the detailed study of the behavior of polymers in between surfaces and the establishment of certain relations describing their macroscopic behavior an important task. A basic macroscopic property to be determined is the force which can be positive or negative expressing net attractions or repulsions between the two surfaces. Bridges formed with at least two monomers of the same chain adsorbed at the two surfaces pull the two surfaces together giving rise to attractive forces which can be measured and used to detect and characterize such bridges. Repulsions on the other hand are due to the osmosis coming from the freedom either of the monomers to expand within the coil dimensions or the chains to expand inside the available

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volume. In the cases where both surfaces attract the chain units competitive to bridges loops are formed due to the adsorption of two units at the same surface which do not contribute to the attractive forces.

The theoretical description of the macroscopic behavior of polymer chains between impenetrable surfaces under conditions where Gaussian chain statistics apply requires incorporation of suitable boundary conditions to take the multiple reflections of the density of the monomers at the two surfaces properly into account. This necessity is even bigger when the surfaces approach to small separations of the order of the radius of gyration of the polymer chains where the problem differs substantially from that of chains interacting with two isolated surfaces. Two types of boundary conditions have been used extensively in the past to describe the behavior of chains in confined geometries. The first called reflecting boundary conditions [6, 7] correspond to the vanishing of the gradient of the probability distribution on the walls and yield extremum flat probabilities to find monomers at the surfaces. The second called absorbing boundary conditions correspond to the vanishing of the probability itself and yield vanishing densities of monomers at the surfaces [8]. Depending on the nature of the interactions both probabilities can be employed to describe chains in the vicinity of surfaces. Starting for example with the reflecting probability with many monomers at the surfaces and including repulsions between monomers and the surfaces we can reach regions of depletion of the density profile of monomers [7]. The same region can also be reached with the absorbing boundary conditions which do not favor finding monomers at the surfaces.

Existing reviews in the field describe both chains near interfaces and chains in between surfaces [9]. The exact distribution function employing absorbing boundary conditions has been used [10] to study both chains in confined geometries and stability of colloids. Studies describing chains fully interacting with the two surfaces include lattice models with a matrix formulation [8, 11] where average chain characteristics as well as density profiles and forces are calculated. Fully interacting chains have also been studied by means of a free energy functional [12] and forces have been found under different solvent conditions. Recently mean field and self consistent field calculations have been used to describe chains with specific interactions [13] where the effects of bridging and looping are discussed. From the experimental side experiments with model systems employing the force apparatus have been performed to study both homopolymers [2, 4] under various solvent conditions but also block copolymers [3-5] of the AB type with only the A block adsorbed at the surfaces. Experiments with the ABA triblock copolymers depending on the size of the adsorbed A block detect repulsive but also simultaneous attractive and repulsive forces.

Previous studies of confined chains with specific interactions do not take into account the proper boundary conditions considering only in an average way the various multiple reflections of the density of the monomers at the walls. We present in this study the macroscopic behavior of Gaussian chains taking into account the multiple reflections within the two surfaces and including specific interactions between the surfaces and the chain ends. In section 2 we discuss the behavior of confined chains under different boundary conditions, in section 3 we introduce the model with specific interactions between the two ends of the chains and the two surfaces and in section 4 a qualitative comparison of the theoretical predictions with experimental results on homopolymers and block copolymers is given.

2. Chains under different boundary conditions.

When the two surfaces are located at the origin and at a positive distance d respectively, the reflecting boundary conditions without any specific interactions yield for the probability to find
the two ends of the chain at the positions \( x_1 \) and \( x_2 \) the infinite sum
\[
P_r(x_1, x_2) = \frac{1}{d} \sum_{n=0}^{\infty} \cos \left( \frac{n \pi x_1}{d} \right) \cos \left( \frac{n \pi x_2}{d} \right) \exp \left( -\frac{\pi^2 \ell^2 N}{6 d^2} n^2 \right),
\]
\[
= \frac{1}{\pi S} \frac{1}{r} \sum_{n=0}^{\infty} \cos (n \pi X_1) \cos (n \pi X_2) \exp \left[ -\left( \frac{n}{r} \right)^2 \right]
\]
\[
X_1 = x_1/d, \quad X_2 = x_2/d,
\]
\[
r = \frac{\sqrt{6} d}{\pi \ell \sqrt{N}} = \frac{d}{\pi S}
\]
reflecting boundary conditions,

(2.1)

representing the large number of reflections of the monomers at the two surfaces. \( X_1 \) and \( X_2 \) varying from 0 to 1 are the reduced distances of the two ends of the chain from the first surface and \( r \) expresses the ratio of the separation \( d \) of the surfaces and the square root of the mean radius of gyration of the chain \( S = \sqrt{(1/6) N \ell^2} \). Because of the addition of all reflections inside the two planes the probability \( P_r(x_1, x_2) \) is normalized in the sense
\[
\int_0^d dx_2 P_r(x_1, x_2) = 1,
\]
as it can be shown straightforwardly from expression (2.1), and the configurational partition function \( C_r \) which is defined as the sum of the probabilities \( P_r \) for all positions of the two ends is simple in this case and equal to:
\[
C_r = \int_0^d dx_1 \int_0^d dx_2 P_r(x_1, x_2) = d.
\]

(2.2)

An interesting observation concerning expression, equation (2.1) is that it is very suitable for quantitative studies since for finite \( r' \)s the proper description of the various properties can be reached taking the first members of the series only. Plotting for example the probability
\[
P_r \pi S = \frac{1}{r} \sum_{n=0}^{\infty} \cos (n \pi X_1) \cos (n \pi X_2) \exp \left[ -\left( \frac{n}{r} \right)^2 \right]
\]
to find the second end of the chain at the reduced distance \( X_2 \) for various locations \( X_1 \) of the first end (Fig. 1), consistency can be reached with the first 10 members of the series. In these plots, left part of figure 1, the flat regions of the probability at the two surfaces implied by the reflecting boundary conditions can be seen. We also see that for large \( r \) the locations of the maxima follow the locations of the fixed first end and this because of the free chain behavior. At smaller distances \( r \) due to the multiple reflections this behavior diminishes and the density tends to be constant everywhere inside the walls.

The force per chain exerted on the plates defined in terms of the derivative with respect to the distance \( d \) can be found in this case by means of equation (2.2) and it is equal to
\[
F = kT \frac{\partial \ln C_r}{\partial d} = \frac{kT}{d},
\]

(2.3)

and positive everywhere. This simple hyperbolic dependence of \( F \) on \( d \), figure 2 (—), is the analogue of the ideal gas law and reveals that though a lot of bridges can be formed with these boundary conditions osmosis is the main dominant effect for these nonlocalized chains. This view can be further supported by means of an increasing localization of the chains where reduction of the osmosis and the appearance of less positive forces are expected to take place.
Fig. 1. — The probability distribution of the reduced position $X_2$ of the second end for various locations $X_1$ of the first end. Left column reflecting boundary conditions, right column absorbing boundary conditions. $X_1 = 0.5$, $X_1 = 0.25$, $X_1 = 0.1$. The heavy line (—) has $X_1 = 0$ for reflecting and $X_1 = 0.01$ for absorbing boundary conditions. The separation distance $r = d/\pi S$ of the surfaces is the same for both figures of the same row.

The trivial example with one of the chain ends localized at any point for which $C_r = 1$ yields zero force revealing a balance between the effects of osmosis and bridges in this case. Localizing the chain more a negative force is expected. Indeed by means of the normalized reflecting probability $P_r(x_1, x_2)/C_r$, we can find and study the probability $P_b$ of a permanent bridge formed with the two chain ends. The two ends of the chain are fixed at the two surfaces so that $x_1 = 0$, $x_2 = d$ and

$$P_b = \frac{P_r(0, d)}{C_r} = \frac{1}{d^2} \sum_{n=0}^{\infty} (-1)^n \exp\left[ - \left( \frac{n}{r} \right)^2 \right],$$

$$r = \frac{\sqrt{6} d}{\pi \ell} = \frac{d}{\pi S}. \quad (2.4)$$
Fig. 2. — Positive or negative forces as a function of the separation \( r \) of the plates for different boundary conditions and degrees of localization. (--- free chains, absorbing boundary conditions), (--- free chain, reflecting boundary conditions), zero force (reflecting, one end localized), (-- reflecting, with the chain ends forming a permanent loop), (--- reflecting, with the chain ends forming a permanent bridge).

The force each bridge exerts is then given by

\[
F_b = kT \frac{\partial \ln P_b}{\partial d} = \frac{kT}{\pi S} \left\{ -\frac{2}{r} + \frac{2}{r^3} \sum_{n=0}^{\infty} (-1)^n n^2 \exp \left[ -\left( \frac{n}{r} \right)^2 \right] \right\} \tag{2.5}
\]

and is plotted also in figure 2 (---). Indeed as expected it is always negative. For the chain to form a loop the two ends should be at one, say the first, surface so we have that

\[
P_l = \frac{P_l(0,0)}{C_r} = \frac{1}{d^2} \sum_{n=0}^{\infty} \exp \left[ -\left( \frac{n}{r} \right)^2 \right] \tag{2.6}
\]

and we take for the force per permanent loop the expression

\[
F_l = kT \frac{\partial \ln P_l}{\partial d} = \frac{kT}{\pi S} \left\{ -\frac{2}{r} + \frac{2}{r^3} \sum_{n=0}^{\infty} n^2 \exp \left[ -\left( \frac{n}{r} \right)^2 \right] \right\} \tag{2.7}
\]

It is again negative (though less negative than that of permanent bridges) figure 2 (---), because while reflecting boundary conditions permit a lot of other pairs of monomers to form bridges the localization coming from the looping at the two ends reduces drastically the osmosis. What we notice is that reflecting boundary conditions yield positive forces when osmosis is dominant, zero forces when the chains are localized with one of their ends and osmosis is partially neutralized, and negative forces accompany localization of both ends which reduces the osmosis even further so that bridge effects become dominant. The delicate cases where both negative and positive forces are simultaneously present as have been seen in experiments need further consideration.

Moving to the absorbing boundary conditions [10], phenomena related to the lack of bridges are expected because monomers are forbidden to touch the surfaces. The probability in this
case can be written as

\[
P_a(x_1, x_2) = \frac{2}{d} \sum_{n=1}^{\infty} \sin \left( \frac{n\pi x_1}{d} \right) \sin \left( \frac{n\pi x_2}{d} \right) \exp \left( -\frac{\pi^2 \ell^2 N}{6 d^2 n^2} \right),
\]

\[
= \frac{2}{\pi S} \frac{1}{r} \sum_{n=1}^{\infty} \sin (n\pi X_1) \sin (n\pi X_2) \exp \left[ -\left( \frac{n}{r} \right)^2 \right]
\]
absorbing boundary conditions.

(2.8)

In figure 1 (right part) the probability \( P_a \) to find the second end of the chain at \( X_2 \) is plotted for various locations \( X_1 \) of the first end. This probability is vanishing at the surfaces regardless of the position of the location of the first end becoming symmetric when the first end is held at the middle of the separating distance. Again we see that for small distances due to the multiple reflections the asymmetry due to the location of the first end at \( X_1 \) tends to disappear. Since no bridges are permitted the force is expected to be positive. By means of the partition function

\[
C_a = \int_0^d dx_1 \int_0^d dx_2 P_a(x_1, x_2) = \frac{2d}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n} (1 - (-1)^n)^2 \exp \left[ -\left( \frac{n}{r} \right)^2 \right],
\]

(2.9)

we find this force which is equal to

\[
F_a = kT \frac{\partial \ln C_a}{\partial d} = \frac{kT}{\pi S} \left[ \frac{1}{r} + \frac{2}{r^3} \sum_{n=0}^{\infty} \frac{1}{n^2} (1 - (-1)^n)^2 \exp \left[ -\left( \frac{n}{r} \right)^2 \right] \right]
\]

(2.10)

and we plot it also in figure 2 (---). It is always positive as expected since no bridges are possible with these boundary conditions.

Summarizing it is interesting to notice that the force is most repulsive for Gaussian chains with absorbing boundary conditions. For reflecting boundary conditions which allow a lot of bridges, the osmosis dominates and positive forces analogous to the ideal gas law are obtained. Localizing one of the chain ends reduces the osmosis and a zero force is possible due to a cancellation of the effects of osmosis and bridging. Localizing both chain ends forming either bridges or loops with chains capable of forming a lot of bridges these bridges dominate osmosis and a negative force is obtained. Notice though the difference between loops and bridges at distance around the square root of the mean end to end square distance of the chain where permanent bridges with the chain ends at opposite surfaces obviously yield more negative forces than permanent loops with the two ends of the chains at the same surface.

In order to see both negative and positive forces together a controlled number of bridges have to be permitted and this will be done in the next section by means of chains with specific interactions.

3. Chains with specific interactions.

In order to have a controlled number of bridges we choose to use the absorbing boundary conditions which correspond to a confinement by an infinite potential and do not favor the touch of the monomers to the surfaces and include specific interactions of the ends of the chain with the surface. We will manage in this way by including attractions between the chain ends and the surfaces to neutralize the effects of the boundary conditions and take a controlled number of bridges. This problem aims at a qualitative description of experiments where
two ends of the chains can be adsorbed at the walls with the same or different sticking energies like the ABC triblocks or the ABA triblocks with the same or different sticking conditions of the end blocks [5]. It aims also to describe situations with chains grafted at one or both surfaces where the sticking energies are much larger, and these though obviously the model only applies rigorously under theta conditions.

Though we can include specific interactions with any specific points of the chain we follow the existing model experiments and choose these points to be the two ends of the chain. The two surfaces called a and b interact with the two ends of the chain called 1 and 2 generally via an interaction potential of the form

\[ V = \exp(-E/kT) \]  for  $0 < y < b$
\[ = 0 \]  for  $y > b$

where $y$ are the distances from the surfaces. Four interaction energies $E_{1a}$, $E_{1b}$, $E_{2a}$, $E_{2b}$ between the two chain ends and the two surfaces and four distances $b_{1a}$, $b_{1b}$, $b_{2a}$, $b_{2b}$ describing the ranges of these interactions are variables which determine the macroscopic behavior of the chains. The usual hard cores of the potentials at small distances are not included since they are taken care of by the absorbing boundary conditions which do not permit the chain points to touch the surfaces. If we include the specific interactions of the ends of the chain the absorbing probability equation (2.8) is modified to

\[ P(x_1, x_2) = \frac{2}{d} \sum_{n=1}^{\infty} \sin \left( \frac{n \pi x_1}{d} \right) \sin \left( \frac{n \pi x_2}{d} \right) \exp \left[ - \frac{[V(x_1) + V(x_2)]}{kT} \right] \exp \left[ - \frac{\pi^2 y^2 N}{6 d^2 n^2} \right], \]

(3.1)

which yields for the partition function $C = \int_0^d dx_1 \int_0^d dx_2 P(x_1, x_2)$ in terms of the reduced energies $\epsilon_{1a} = E_{1a}/kT$, $\epsilon_{1b} = E_{1b}/kT$, $\epsilon_{2a} = E_{2a}/kT$, $\epsilon_{2b} = E_{2b}/kT$ and the reduced distances $\beta_{1a} = b_{1a}/S$, $\beta_{1b} = b_{1b}/S$, $\beta_{2a} = b_{2a}/S$, $\beta_{2b} = b_{2b}/S$, the expression

\[ C = \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} A_1 \cdot A_2 \exp \left[ - \left( \frac{n}{r} \right)^2 \right], \]

\[ A_1 = \left\{ \exp(-\epsilon_{1a}) - 1 \right\} \cos (nb_{1a}/S) - \exp(-\epsilon_{1a}) - (-1)^\alpha \left\{ \exp(-\epsilon_{1b}) - 1 \right\} \cos (nb_{1b}/S), \]

\[ A_2 = \left\{ \exp(-\epsilon_{2a}) - 1 \right\} \cos (nb_{2a}/S) - \exp(-\epsilon_{2a}) - (-1)^\alpha \left\{ \exp(-\epsilon_{2b}) - 1 \right\} \cos (nb_{2b}/S), \]

(3.2)

The force per chain $F = kT \frac{\partial \ln C}{\partial d}$ can then be found and it is equal to

\[ F = \frac{1}{kT \pi S} \left\{ \frac{1}{r} + \sum_{n=1}^{\infty} \exp \left[ - \left( \frac{n}{r} \right)^2 \right] \left[ \frac{2}{r^2} A_1 \cdot A_2 + \frac{1}{n} D_1 \cdot A_2 + \frac{1}{n} A_1 \cdot D_2 \right] \right\} \]

(3.3a)
where $D_1$ and $D_2$ come from the derivatives of $A_1$ and $A_2$ with respect to $d$ and are given by

$$D_1 = \frac{b_{1a}}{r} \left[ \exp(-\varepsilon_{1a}) - 1 \right] \sin \left( \frac{n\beta_{1a}}{r} \right) - (-1)^n \frac{b_{1b}}{r} \left[ \exp(-\varepsilon_{1b}) - 1 \right] \sin \left( \frac{n\beta_{1b}}{r} \right)$$

$$D_2 = \frac{b_{2a}}{r} \left[ \exp(-\varepsilon_{2a}) - 1 \right] \sin \left( \frac{n\beta_{2a}}{r} \right) - (-1)^n \frac{b_{2b}}{r} \left[ \exp(-\varepsilon_{2b}) - 1 \right] \sin \left( \frac{n\beta_{2b}}{r} \right).$$

(3.3b)

Expression (3.3) furnishes the force as a function of the characteristics of the chain which are its radius of gyration $S$, the reduced distance $r = \frac{d}{\pi S}$ of the two surfaces and the characteristics of the interactions between the ends of the chains and the surfaces which in the model are the four energies $\varepsilon_{1a}$, $\varepsilon_{1b}$, $\varepsilon_{2a}$, $\varepsilon_{2b}$ and the four ranges of these interactions $\beta_{1a}$, $\beta_{1b}$, $\beta_{2a}$, $\beta_{2b}$, respectively. Equation (3.3) can be employed for many studies. More negative forces indicate more bridges which compete with loops while positive forces come from the osmosis.

Though the force $F$ depends on 4 different interaction energies the variation of which can describe many different situations we choose to study a few specific cases which will give us a thorough insight in the general behavior of the force as a function of the interaction energies. The surface separation is taken to be $r = 1.5$ where the minima of the negative forces lie (see Fig. 4), and all $\beta$'s are assigned the relatively high value of 0.3 in order to resemble the case of adsorbed blocks for block copolymers, see section 4. The first choice is the combination:

$$\varepsilon_{1a} = \varepsilon, \quad \varepsilon_{1b} = -\varepsilon, \quad \varepsilon_{2a} = -\varepsilon, \quad \varepsilon_{2b} = \varepsilon.$$  

(3.4a)

In this case, taking $\varepsilon$ large negative, the first end of the chain is strongly attracted to the surface while the second end is strongly attracted to the surface $b$. Under these conditions a high probability of forming bridges is expected and therefore the appearance of a negative force. In figure 3 (—) the force $F$ for this combination is plotted as a function of $\varepsilon$ and negative forces are indeed observed. For smaller values of attraction $\varepsilon$, bridges are not dominant and the force becomes positive. The combination equation (3.4a) represents also the symmetrical case for positive values of $\varepsilon$ with ends adsorbed at the opposite surfaces. In the case where all energies are equal

$$\varepsilon_{1a} = \varepsilon, \quad \varepsilon_{1b} = \varepsilon, \quad \varepsilon_{2a} = \varepsilon, \quad \varepsilon_{2b} = \varepsilon,$$

(3.4b)

Fig. 3. — Attractive and repulsive forces as a function of the reduced energy $\varepsilon$. (— two ends form bridges, $\varepsilon_{1a} = \varepsilon, \varepsilon_{1b} = -\varepsilon, \varepsilon_{2a} = -\varepsilon, \varepsilon_{2b} = \varepsilon$), (— the two ends equally attracted or repulsed from the surfaces, $\varepsilon_{1a} = \varepsilon, \varepsilon_{1b} = \varepsilon, \varepsilon_{2a} = \varepsilon, \varepsilon_{2b} = \varepsilon$), (— the two ends form loops, $\varepsilon_{1a} = \varepsilon, \varepsilon_{1b} = -\varepsilon, \varepsilon_{2a} = \varepsilon, \varepsilon_{2b} = -\varepsilon$), (— opposite interactions for the two ends, $\varepsilon_{1a} = \varepsilon, \varepsilon_{1b} = \varepsilon, \varepsilon_{2a} = -\varepsilon, \varepsilon_{2b} = -\varepsilon$), $b = 0.3$, $r = 1.5$. 

![Fig. 3. — Attractive and repulsive forces as a function of the reduced energy $\varepsilon$. (— two ends form bridges, $\varepsilon_{1a} = \varepsilon, \varepsilon_{1b} = -\varepsilon, \varepsilon_{2a} = -\varepsilon, \varepsilon_{2b} = \varepsilon$), (— the two ends equally attracted or repulsed from the surfaces, $\varepsilon_{1a} = \varepsilon, \varepsilon_{1b} = \varepsilon, \varepsilon_{2a} = \varepsilon, \varepsilon_{2b} = \varepsilon$), (— the two ends form loops, $\varepsilon_{1a} = \varepsilon, \varepsilon_{1b} = -\varepsilon, \varepsilon_{2a} = \varepsilon, \varepsilon_{2b} = -\varepsilon$), (— opposite interactions for the two ends, $\varepsilon_{1a} = \varepsilon, \varepsilon_{1b} = \varepsilon, \varepsilon_{2a} = -\varepsilon, \varepsilon_{2b} = -\varepsilon$), $b = 0.3$, $r = 1.5$.](image-url)
negative forces are found when the ends are attracted strongly enough and positive ones for positive energies where the ends are repulsed away from the surfaces and osmosis is dominant (Fig. 3 (—)). Another class of behavior for $F$ as a function of $\varepsilon$ is found for the case

$$
\varepsilon_{1a} = \varepsilon, \quad \varepsilon_{1b} = -\varepsilon, \quad \varepsilon_{2a} = \varepsilon, \quad \varepsilon_{2b} = -\varepsilon.
$$

(3.4c)

It is again a symmetrical case for which now both ends of the chain are adsorbed at the same surfaces, the chains form loops and since no other bridges are allowed because of the boundary conditions a positive force is observed (Fig. 3 (—)). Finally, in figure 3 (—) we also plot the case with

$$
\varepsilon_{1a} = \varepsilon, \quad \varepsilon_{1b} = \varepsilon, \quad \varepsilon_{2a} = -\varepsilon, \quad \varepsilon_{2b} = -\varepsilon,
$$

(3.4d)

where the one end is equally attracted by the two surfaces while the other is equally repulsed by them, no bridges are favor in this case, and the dominant osmosis give positive forces.

Having obtained a general idea of the interaction conditions which yield positive or negative forces, summarized in the force-energy diagrams shown in figure 3, we proceed to study the behavior of the force as a function of $r$, the reduced distance between the plates. We pick up four cases related to the previous analysis where the various effects can be seen. Taking the energies

$$
\varepsilon_{1a} = -8, \quad \varepsilon_{1b} = 8, \quad \varepsilon_{2a} = 8, \quad \varepsilon_{2b} = -8
$$

(3.5a)

for which bridges are favored, the force is of the structure shown in figure 4 (—). For small distances the large density of monomers within the plates due to the multiple reflections produces a high monomer osmosis which causes a positive force in agreement with other theoretical results on single chains [14] but also in accord with the experimental results on polymer solutions, polymer melts [15] and solid polyme films [16]. This force decreases for larger distances, changes sign and reaches a minimum at distances larger than its radius of gyration related with the mean end to end square distance of the chain where the effects of the bridges are maximum [17]. Finally it increases again at larger distances where larger freedom of the chains increase their chain osmosis. Notice the positive vanishing of these forces at large distances even when attractive minima are present (Fig. 4b), which agrees with the experimental observations. Decreasing the attractions to the values

$$
\varepsilon_{1a} = -6, \quad \varepsilon_{1b} = 6, \quad \varepsilon_{2a} = 6, \quad \varepsilon_{2b} = -6,
$$

(3.5b)

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{Force as a function of the separation of the two surfaces: (— bridges with $\varepsilon_{1a} = -8$, $\varepsilon_{1b} = 8$, $\varepsilon_{2a} = 8$, $\varepsilon_{2b} = -8$), (— bridges with $\varepsilon_{1a} = -6$, $\varepsilon_{1b} = 6$, $\varepsilon_{2a} = 6$, $\varepsilon_{2b} = -6$), (— loops with $\varepsilon_{1a} = -4$, $\varepsilon_{1b} = 4$, $\varepsilon_{2a} = -4$, $\varepsilon_{2b} = 4$), (— osmosis with $\varepsilon_{1a} = 5$, $\varepsilon_{1b} = 5$, $\varepsilon_{2a} = 5$, $\varepsilon_{2b} = 5$), $b = 0.3$. The forces always vanish from positive values, figure 4b.}
\end{figure}
reduces the minimum of the force figure 4 (—). Moving to the next combination of interactions the values

\[ \varepsilon_{1a} = -4, \quad \varepsilon_{1b} = 4, \quad \varepsilon_{2a} = -4, \quad \varepsilon_{2b} = 4. \]  

(3.5c)

are taken. For this combination loops are important and the force is always positive, figure 4 (—). Finally for the values

\[ \varepsilon_{1a} = 5, \quad \varepsilon_{1b} = 5, \quad \varepsilon_{2a} = 5, \quad \varepsilon_{2b} = 5. \]  

(3.5d)

the ends of the chains are kept away from the surfaces and osmosis is the dominant effect. The force in this case shown in figure 4 (—) is always positive.

Of interest is the comparison of the average numbers of bridges and loops given by the ratio of their two probabilities. The probability \( P_b \) to form a bridge is given by

\[ P_b = P(x_1 = \delta, x_2 = d - \delta) + P(x_1 = d - \delta, x_2 = \delta) \]

while the probability \( P_l \) to form a loop is given by

\[ P_l = P(x_1 = \delta, x_2 = \delta) + P(x_1 = d - \delta, x_2 = d - \delta) \]

where \( \delta \) tends to zero. And though these probabilities are small because of the boundary conditions their ratio is finite and equal to

\[ \frac{P_b}{P_l} = E \cdot D \]

with

\[ E = \frac{\exp(-\varepsilon_{1a} - \varepsilon_{2b}) + \exp(-\varepsilon_{2a} - \varepsilon_{1b})}{\exp(-\varepsilon_{1a} - \varepsilon_{2a}) + \exp(-\varepsilon_{1b} - \varepsilon_{2b})} \]

and

\[ D = \frac{\sum_{n=1}^{\infty} (-1)^{n+1} n^2 \exp\left[-\left(\frac{n}{r}\right)^2\right]}{\sum_{n=1}^{\infty} n^2 \exp\left[-\left(\frac{n}{r}\right)^2\right]} \]  

(3.6)

This ratio depends on two factors. The first \( E \) factor is energy dependent and it is larger or smaller than 1, favoring bridges or loops depending on the values of the energies of interaction (Fig. 5). The second \( D \) is a distance dependent factor and its plot is shown also in figure 5, it is similar to that found by lattice calculations [8] for the fully interacting chains. We notice that disregarding the energy factor which can change the relative population, loops and bridges are equally favorable for small distances where many reflections of the chains permit the formation of both. Increasing the separation of the plates, a characteristic distance is reached where bridging is reduced drastically compared to looping due to the limited extension of the chains.

We can also give a systematic dependence of \( F \) on the ranges \( b \) of interactions by plotting \( F \) when all ranges are equal for the characteristic cases discussed before (Fig. 6). This dependence is useful in the cases where the width of the adsorbed layer varies. Such a variation can be achieved in practice for ABA block copolymers by varying the molecular weight of the adsorbed A blocks. All lines start at the same point of zero range where no interactions exist. Heavy (—) and normal (—) lines correspond to the combinations yielding bridges. For larger
Fig. 5. — The ratio of the probabilities of bridges to loops. The energy factor $E$ for the combination of energies ($\epsilon_{1a} = \epsilon$, $\epsilon_{1b} = -\epsilon$, $\epsilon_{2a} = -\epsilon$, $\epsilon_{2b} = \epsilon$) favoring bridges (---) and for the combination $\epsilon_{1a} = \epsilon$, $\epsilon_{1b} = -\epsilon$, $\epsilon_{2a} = \epsilon$, $\epsilon_{2b} = -\epsilon$) favoring loops (---). The distance factor $D$ depends on $r$ and diminishes drastically around $r = 1$.

Fig. 6. — The dependence of the force $F$ on the range $b$ of interactions: (--- bridges with $\epsilon_{1a} = -8$, $\epsilon_{1b} = 8$, $\epsilon_{2a} = 8$, $\epsilon_{2b} = -8$). (--- bridges with $\epsilon_{1a} = -6$, $\epsilon_{1b} = 6$, $\epsilon_{2a} = 6$, $\epsilon_{2b} = -6$). (--- loops with $\epsilon_{1a} = 4$, $\epsilon_{1b} = -4$, $\epsilon_{2a} = 4$, $\epsilon_{2b} = 4$). (--- osmosis with $\epsilon_{1a} = 5$, $\epsilon_{1b} = 5$, $\epsilon_{2a} = 5$, $\epsilon_{2b} = 5$), $r = 1.5$.

attractions more negative forces are observed. The dashed line corresponds to loops and it is always positive while the dotted line of positive repulsions correspond to osmosis and yields always positive forces.

4. Comparison with experiments.

The present exact study is limited to a linear chain considered as a representative of an ensemble of many chains and does not include two body interactions representing thus the theta or dense states. Excluded volume interactions could be incorporated and describe quantitatively in the known approximate schemes good and subtheta conditions and also concentration effects by means of chain-chain interactions. The comparison though of the present results with the existing experiments of polymers in solution and melts which shows the capability of this single chain treatment to produce at least in a qualitative way the main effects, is of interest. Our aim is primarily to show how certain features found experimentally can be reproduced by the present model and to reveal the basic underlying mechanisms. The coexistence of positive and negative forces due to a controlled number of bridges as well as a positive vanishing of all these forces at the limit of large separations of the surfaces agree well with the experimental observations. The increasing value of the force $F$ for larger molecular...
weights of nonadsorbed chains seen by experiments is also well reproduced by the present model. Indeed larger values of the molecular weight $N$ give smaller reduced distances $r = \sqrt{6} \frac{d}{\pi \ell} \sqrt{\frac{N}{r}}$ and in case of positive forces larger positive values of them, figures 4, 7, 8.

Experiments with AB diblock copolymers have been performed [3, 4, 18] where the A block with molecular weight $N_A$ is adsorbed at the surfaces while the B block of molecular weight $N_B$ is not adsorbed. Positive forces are always observed and they increase with the molecular weight $N_B$ of the nonadsorbed block while they are smaller for larger molecular weights $N_A$ of the adsorbed block. An interesting analogy of this specific class of diblock copolymers can be provided, realizing of course that our model strictly corresponds only to the low coverage unstretched situation. According to the present model the AB diblock with the A block adsorbed can be represented with a chain of length $N_B$ whose one end interacts with the surfaces, $\varepsilon_{1a} = \varepsilon_{1b} = -\varepsilon$ with sticking energy which increases with the molecular weight of the adsorbed block while the second end of the chain does not interact, $\varepsilon_{2a} = \varepsilon_{2b} = 0$. Indeed for this case the forces are always positive (Fig. 7). Increasing the molecular weight $N_B$ of the nonadsorbed block the magnitude of the force increase because as in the case of homopolymers $r$ decreases. But also increasing $N_A$ of the adsorbed block $\varepsilon$ increases and less positive forces are observed (Fig. 7), similar to experimental findings.

Fig. 7. — The force of a block copolymer for which only one block is adsorbed ($\varepsilon_{1a} = \varepsilon_{1b} = -\varepsilon$, $\varepsilon_{2a} = \varepsilon_{2b} = 0$), as a function of sticking energy $\varepsilon$, $r = 1.5$, and separation distance $r$ for $\varepsilon = -6$ (—) and $\varepsilon = -2$ (—), $b = 0.3$ for both cases.

Another insight which the present model can provide concerns the results of experiments with triblock copolymers. It was found that triblocks with larger sticking blocks and larger sticking energies do not show attractive forces though similar triblocks with smaller sticking blocks do [5]. This was explained by means of the larger probability of forming loops at the initial surface for larger sticking energies. The experiments performed with these polymers consist of an initial surface with adsorbed polymer chains and a second approaching bare surface. The system is not at equilibrium so the initial surface interacts to a larger extend with the end blocks of the triblock chains than the oncoming one. In the present model this asymmetry of the sticking energies can be chosen to be described with the combination

$$
\varepsilon_{1a} = -6 - \varepsilon, \quad \varepsilon_{1b} = -6, \quad \varepsilon_{2a} = -6 - \varepsilon, \quad \varepsilon_{2b} = -6.
$$

For positive values of $\varepsilon$ all the energies are attractive but their value for the two surfaces is different and the difference increases with $\varepsilon$. The plot of the force $F$ as a function of $\varepsilon$ at a separation distance $r = 0.9$ and $\beta = 0.3$ is seen in figure 8. Increasing $\varepsilon$ the repulsive character of $F$ increases and this demonstrates how different sticking block and sticking energies are capable to yield both negative forces for small $\varepsilon$ and positive ones for larger $\varepsilon$. As a matter of
Fig. 8. — The repulsive character of the forces increases with the difference $\varepsilon$ of the attractions from the two surfaces, left, $r = 0.9$. For much larger attractions ($\varepsilon \to \infty$) from one plane no negative forces are possible, right. $b = 0.3$ for both cases.

In this region the force becomes

\[
F = \frac{1}{kT} \pi S \left[ \frac{1}{r} + \sum_{n=1}^{\infty} \frac{\exp \left( - \left( \frac{n}{r} \right)^2 \right)}{n^2} \left( \cos \left( \frac{n\beta}{r} \right) - 1 \right)^2 \right]^{\varepsilon_{1a}, \varepsilon_{2a} \to \infty}
\]

\[
\frac{1}{r} \sum_{n=1}^{\infty} \frac{1}{n^2} \left( \cos \left( \frac{n\beta}{r} \right) - 1 \right)^2 \exp \left[ - \left( \frac{n}{r} \right)^2 \right]^{\varepsilon_{1b}, \varepsilon_{2b} \text{ finite}} \quad (4.1)
\]

which is always positive as can be seen from figure 8, where it is plotted as a function of $r$.

5. Conclusions.

The force per chain between two impenetrable plane surfaces enclosing polymers has been studied in detail taking into account all multiple reflections. Osmosis either of monomers or chains yield positive repulsive forces while bridges which compete with loops yield negative attractive forces. For absorbing boundary conditions including specific interactions between the chain ends and the surfaces the number of bridges can be controlled and both positive and negative forces are possible. The ratio of the numbers of bridges and loops is equal to the product of an energy dependent and a distance dependent factor and can be varied in a prescribed way. The analytic expressions describing the macroscopic behavior of systems of various types of chains enclosed between the same or different surfaces are qualitatively in agreement with various up to date experiments. This indicates that common features are responsible for the observed behavior and the theoretical predictions. Despite the obvious simplified description compared to the real experimental situation, this suggests that these calculations may be helpful as a guide for future experiments. Two body interactions to study good and poor solvent effects and chain-chain interactions for the study of concentration effects can be incorporated to both linear but also to chains of other architectures.

Acknowledgments.

We would like to thank Dr. C. Topragioglou, and Mrs. E. Manias and G. Belder for useful discussions on the subject. This work was made possible by financial support from the
Nederlandse Organisatie voor Wetenschappelijk Onderzoek (Netherlands Organization for the Advancement of Research, NWO).

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