

Surface forces induced by ideal equilibrium polymers

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The behavior of a dilute solution of ideal equilibrium (or “living”) polymers confined between two surfaces and the effect on the surface forces are investigated theoretically. Exact analytical expressions are obtained for the concentration profile and the average length of chains in the gap, the adsorbed amount, and the disjoining pressure for chains with an arbitrary interaction with the surfaces. If the adsorption energy of the segments increases, the excess amount of segments in the gap and the average chain length increase and diverge continuously at a critical value of the adsorption energy which depends on the average length of the chains in the bulk and on the width of the gap. If the chain ends have no specific interaction with the surfaces, the equilibrium polymers cause an attraction between the surfaces, either via the depletion mechanism in the case of nonadsorbing polymers or via the formation of bridges in the case of adsorbing polymers. If only one of the functional groups adsorbs preferentially on the surface, the interaction becomes repulsive (if the main-chain segments do not adsorb), due to steric repulsion. On the other hand, if both functional groups adsorb preferentially, the interaction is attractive as a result of the formation of bridges with one adsorbed end on either surface. © 2003 American Institute of Physics.
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I. INTRODUCTION

It is well known that the addition of polymers to a colloidal system modifies the interactions between the colloidal particles.^{1–3} This is important for many technological applications, such as the production of paints, coatings, and food products. Polymers can affect the colloidal stability via several mechanisms. If the polymers do not adsorb on the colloidal particles, they usually cause attraction between the particles.^{1,4} The origin of this effect, called depletion attraction, is the loss of conformational entropy of a polymer chain when it is confined between two particles. If this entropy loss is not compensated by a gain in adsorption energy, the polymers avoid the region between the particles, and the unbalanced osmotic pressure of the bulk then pushes the particles together. If the polymers do adsorb on the particle surface, both attraction and repulsion can be observed, depending on the experimental conditions.¹ Under full equilibrium conditions, the interaction is attractive due to the formation of bridges. Experimentally it is known, however, that polymer adsorption can also stabilize dispersions. The latter is due to steric repulsion between polymer layers, and occurs only in nonequilibrium situations, when the polymers are adsorbed so strongly that no exchange with the bulk solution takes place on the time scale of a particle encounter.

More recently, there has been interest in telechelic polymers, which contain one or more groups that can adsorb strongly on the particle surface.^{5–10} Examples of these are block copolymers with one or more adsorbing blocks, or hydrophobically modified water-soluble polymers. When a chain has only one adsorbing group, it causes repulsion be-

tween two surfaces due to steric hinderance. On the other hand, when the chains have two or more adsorbing groups, there are several possibilities. The chains can either form loops, which give a repulsive contribution to the interaction between two surfaces, or they can form bridges, which give an attractive contribution. It has been shown theoretically that the competition between these two effects can result in an attractive minimum in the interaction curve of order kT per chain.^{5–8} For this reason, telechelic polymers are used widely as thickeners in, for example, the coatings industry.

An interesting development in recent years has been the design of so-called supramolecular polymers. These are linear chains of small molecules held together by noncovalent, reversible interactions, such as hydrogen bonds.^{11–15} They are also referred to as “equilibrium polymers” or “living polymers,” and have much in common with other living polymers, such as wormlike micelles.^{16,17} In many aspects they behave as conventional polymers, but they also introduce distinctly new features, because the bonds between monomers can break and recombine on experimental time scales. The equilibrium between the formation and breakage of bonds results in a polydisperse distribution of chain lengths. This distribution is not fixed but it responds to variable conditions such as the monomer concentration, the temperature, and the presence of external fields, e.g., those arising from shear or from a surface.

Equilibrium polymers may be very interesting for the use in colloidal systems, because their properties can be tuned rather easily. For example, by applying shear some of the chains may break. This may result in interesting rheological behavior, such as pronounced shear thinning and thixotropy. Relatively little is known about the effect of equilibrium polymers on colloidal stability. Most theoretical

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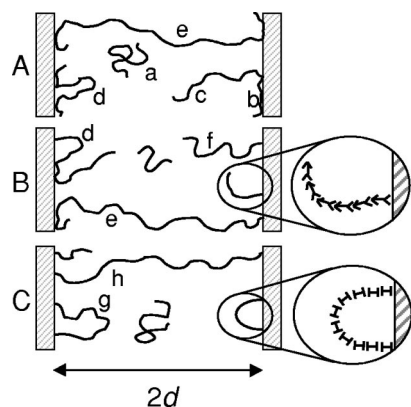


FIG. 1. A schematic representation of equilibrium polymers between two surfaces. (A) Chains without preferentially adsorbing functional groups ("sticky ends"). (B) Chains with one sticky end; the magnification shows schematically a chain of "directional" monomers of which only the acceptor group sticks to the surface. (C) Chains with two sticky ends; the magnification shows schematically a chain of "nondirectional" monomers with two identical bonding groups that stick to the surface (note that this situation applies also to "directional" chains if both the acceptor and the donor group stick to the surface). Classes of conformations are indicated: (a) free chain; (b) train; (c) tail; (d) loop; (e) bridge; (f) end-adsorbed chain; (g) end-to-end loop; (h) end-to-end bridge. Note that for adsorbing chains ($c > 0$) loops and bridges may occur also without special sticky end groups [e.g., (d), (e)].

investigations so far have considered only the case of non-adsorbing equilibrium polymers.^{18–20} These lead to a depletion interaction, similar to that of a polydisperse solution of conventional polymers. Adsorbing equilibrium polymers have received only very little attention.²¹ Recently, we have investigated the effect of supramolecular polymers that adsorb with their end-groups on the surface.²² At both ends of a supramolecular polymer chain there is a free functional group (unless the chain is in a cyclic conformation). These functional groups will generally have an interaction with the surface different from the segments in the middle of the chain. For example, if the bonds between monomers are based on hydrogen bonding, the functional groups can bind strongly to surfaces with hydrogen bond acceptor or donor groups. We found that the sign of the interaction between two surfaces covered with layers of end-adsorbed supramolecular polymers depends on the directionality of the polymer chains. Chains that are formed by symmetric "B–B" monomers (where B denotes a self-complementary bonding group) give rise to attractive forces, because they can form bridges between two particles [see Fig. 1(C)]. This is similar to the effect of telechelic polymers with two adsorbing groups. On the other hand, chains of asymmetric "A–D" monomers (where A and D denote a complementary acceptor and donor group, respectively) give rise to steric repulsion if only one of the two functional groups adsorbs. These chains behave similarly to telechelic polymers with one adsorbing group [Fig. 1(B)].

In this paper we investigate the effect of equilibrium polymers on colloidal stability in more detail. We consider both adsorbing and nonadsorbing equilibrium polymers confined between two flat surfaces and calculate the concentration profile of polymers in the gap, their average length, and the pressure on the surfaces brought about by the polymers.

In Sec. II we briefly summarize the statistical thermodynamics of equilibrium polymers in a homogeneous bulk solution. The statistics of polymer chains confined between two surfaces are described in Sec. III. We use the Gaussian chain approximation for the polymers, which is a good approximation for dilute solutions under theta conditions and for low adsorption densities. The behavior of confined equilibrium polymers with arbitrary interaction with the surfaces is described in Sec. IV. In Sec. V we consider the effect of chains of which one or both ends adsorb specifically on the surface. In this paper we will always assume that the interactions between the surfaces are brought about under full equilibrium conditions. This is the most relevant situation if the bonds between the monomers break and recombine rapidly compared to the time scale of a particle encounter.

II. EQUILIBRIUM POLYMERS IN A HOMOGENEOUS SOLUTION

The chain length distribution of equilibrium polymers in a homogeneous solution can be calculated using statistical thermodynamics. For a system of ideal equilibrium polymers, the free energy F_0 can be written as^{16,28}

$$\frac{F_0}{VkT} = \int_0^\infty \rho_0(N) \left[\ln \rho_0(N) - 1 + \frac{E}{kT} \right] dN, \quad (1)$$

where V is the volume, k is Boltzmann's constant, T the temperature, $\rho_0(N)$ the number density of chains of length N , and E the (free) energy cost of creating two chain ends (often called the scission energy or the end-cap energy). The formation of closed rings is neglected in this approach. We assume here that the chain length N is a continuous variable. This is justified if the average length is much larger than the length of one monomer. The subscript 0 is used to denote that the system is homogeneous. The minimization of Eq. (1) with respect to $\rho_0(N)$ under the constraint of monomer conservation,

$$\int_0^\infty \rho_0(N) N dN = \rho_0, \quad (2)$$

with ρ_0 the total number concentration of segments, yields an exponential chain length distribution:

$$\rho_0(N) = \frac{\rho_0}{\langle N_0 \rangle^2} \exp\left(-\frac{N}{\langle N_0 \rangle}\right). \quad (3)$$

The number-averaged chain length $\langle N_0 \rangle$ depends on the segment concentration and the scission energy:

$$\langle N_0 \rangle = \sqrt{\rho_0} \exp\left(\frac{E}{2kT}\right), \quad (4)$$

which is valid for $\langle N_0 \rangle \gg 1$. We note that exactly the same result is found for chains with excluded-volume interactions within a mean-field approximation. Adding a mean-field interaction term (which depends only on the total concentration ρ_0) to Eq. (1) has no effect on $\rho_0(N)$.¹⁶

We can also obtain the chemical potential μ and the osmotic pressure Π from Eq. (1):

$$\mu = \left(\frac{\partial F_0}{\partial n_0} \right)_{V,T} = - \frac{kT}{\langle N_0 \rangle},$$

$$\Pi = - \left(\frac{\partial F_0}{\partial V} \right)_{n_0,T} = \frac{\rho_0 kT}{\langle N_0 \rangle},$$
(5)

where $n_0 = \rho_0 V$ is the total number of monomers in a volume V .

III. STATISTICS OF CONFINED MACROMOLECULES

The presence of a surface affects a polymer chain in two ways: it reduces the conformational entropy of the chain and it may have an energetic interaction with the polymer segments. If the adsorption energy of the segments is high enough to compensate the entropy loss of a polymer chain, the chains adsorb on the surface. On the other hand, if the adsorption energy is not sufficient to compensate the entropy loss, the chains avoid the region near the surface (depletion). A variety of methods has been used to describe polymer chains near a surface. Here we use the relatively simple Gaussian chain approximation, in which all interactions between different chain segments are neglected. Within this approximation analytical expressions can be obtained for the distribution function of a polymer chain confined between two walls.²³ In this section we briefly summarize some properties of confined Gaussian chains.

An important quantity describing the statistics of a polymer chain is the distribution function $G(z, z', N)$ which gives the statistical weight of a (sub)chain of N Kuhn segments beginning at z' and ending at z (here z and z' denote coordinates in the direction normal to the surfaces). The distribution function $G(z, z', N)$ satisfies the zero-field Edwards equation:²⁴

$$\frac{b^2}{6} \frac{\partial^2 G}{\partial z^2} = \frac{\partial G}{\partial N},$$
(6)

where b is the segment (or Kuhn) length, i.e., the mean random walk step length. The initial condition specifies the starting point of the chain:

$$G(z, z', 0) = \delta(z - z').$$
(7)

For polymer chains in free space the solution of the Edwards equation is the well known Gaussian distribution. In the case of confined polymer chains, we need to account for the interactions with the surfaces. We assume that the adsorption potential near both surfaces is short-ranged. It has been shown²⁵ that the existence of such a potential is equivalent to the application of the following boundary conditions:

$$\left[\frac{1}{G} \frac{\partial G}{\partial z} \right]_{z=0} = - \left[\frac{1}{G} \frac{\partial G}{\partial z} \right]_{z=2d} = -c.$$
(8)

Here, $z = 0$ and $z = 2d$ are the positions of the surfaces. The parameter c is the inverse of the so-called extrapolation length. It specifies the interactions of the segments with the surface. In the case of depletion (nonadsorbing surface) $c < 0$, whereas in the case of adsorption $c > 0$. At the adsorption/depletion transition $c = 0$. The adsorption parameter c can be related to the adsorption energy of the polymer

segments and the temperature.^{26,10} Close to the adsorption threshold c varies as $c \sim (\chi_s - \chi_{sc})$ where $\chi_s = -(u_p^a - u_0^a)/kT$ is the difference between the adsorption energy of a polymer segment u_p^a and that of a solvent molecule u_0^a , and χ_{sc} is the value of χ_s at the adsorption/depletion transition (where the adsorption energy is just sufficient to compensate the entropy loss of a chain). For $\chi_s < \chi_{sc}$ ($c < 0$) the polymers are depleted, whereas for $\chi_s > \chi_{sc}$ ($c > 0$) the polymers adsorb. In the case of adsorption, c^{-1} is a measure for the thickness of the adsorption layer formed by the macromolecules. For small c (weak adsorption), the adsorbed layer is fluffy with many loops, whereas for $c \gg 1$ the layer is compact with most segments adsorbed in trains.

The solution of the Edwards equation with boundary conditions (7) and (8) has been derived in the context of heat conduction,²⁷ and it was applied to the case of polymer adsorption by Gorbunov and Skvortsov in order to develop a theory for polymer chromatography:²³

$$G(z, z', N) = \frac{1}{d} \sum_{m=1}^{\infty} \frac{\sin\left(\alpha_m \xi - \frac{m\pi}{2}\right) \sin\left(\alpha_m \xi' - \frac{m\pi}{2}\right)}{1 - \lambda/(\alpha_m^2 + \lambda^2)} \times \exp\left[-\left(\frac{\alpha_m R}{d}\right)^2\right],$$
(9)

where

$$\xi = \frac{z-d}{d}, \quad \xi' = \frac{z'-d}{d}, \quad \lambda = cd, \quad \text{and} \quad R = b \sqrt{\frac{N}{6}}.$$
(10)

Here ξ and ξ' are the reduced distances between the chain ends and the middle of the slit ($z = d$), λ is a dimensionless adsorption parameter (or a dimensionless half-distance between the surfaces) defined as the ratio between the half gap width and the extrapolation length $1/c$, and R is the radius of gyration of a chain of length N (note that we express the chain length in the number of Kuhn segments). The eigenvalues α_m are the positive roots of

$$(\alpha_m \tan \alpha_m + \lambda)(\alpha_m \cot \alpha_m - \lambda) = 0.$$
(11)

For a nonadsorbing surface ($\lambda < 0$) all eigenvalues are real. For an adsorbing surface ($\lambda > 0$) on the other hand, the first eigenvalue is imaginary, and if $\lambda > 1$ also the second eigenvalue is imaginary.

In Secs. IV and V we use the distribution function $G(z, z', N)$ to describe equilibrium polymers, with an exponential chain-length distribution (see Sec. II), confined between two surfaces.

IV. EQUILIBRIUM POLYMERS IN A GAP

A. Statistical thermodynamics

In this section we consider confined equilibrium polymers of which the two functional groups have no special interactions with the surfaces [Fig. 1(A)]. Chains of which the ends adsorb preferentially (“sticky ends”) will be considered in Sec. V. We consider a solution of equilibrium polymers confined between two surfaces of area A separated by a distance $2d$. The area A is taken infinitely large, so that

edge effects can be ignored. The interactions of the segments with the surface are taken into account by the adsorption parameter c . We assume that the solution in the gap is in equilibrium with a reservoir of constant monomer concentration ρ_0 (and hence chemical potential μ and osmotic pressure Π). Under these conditions, the thermodynamic equilibrium situation is determined by a minimum of the grand potential:¹⁸

$$\frac{\Omega}{kT} = V \int_0^\infty \rho(N, d) \left[\ln \rho(N, d) - 1 + \frac{E}{kT} - \ln Z(N, d) - \frac{\mu N}{kT} \right] \times dN + \frac{\Pi V}{kT}, \quad (12)$$

where $V = 2Ad$ is the volume. The chemical potential μ and the osmotic pressure Π account for equilibrium with the bulk solution. They are given by Eq. (5). The term $\ln Z(N, d)$ accounts for the confinement of the chain and the interactions with the surface. Here $Z(N, d)$ is the partition function of a chain of length N confined between two surfaces at separation $2d$. It can be obtained from Eq. (9) by integration over the positions of the two end-points:²³

$$Z(N, d) = \frac{1}{2d} \int_0^{2d} \int_0^{2d} G(z, z', N) dz dz'. \quad (13)$$

The chain length distribution in the gap can be obtained by the minimization of Eq. (12) with respect to $\rho(N, d)$. This yields

$$\rho(N, d) = Z(N, d) \rho_0(N), \quad (14)$$

where $\rho_0(N)$ is the concentration of chains of length N in a homogeneous isotropic bulk solution that is in equilibrium with the solution in the gap. It is given by Eq. (3). Substitution in Eq. (12) gives for the grand potential in the equilibrium situation:

$$\frac{\Omega}{kT} = -V \int_0^\infty \rho(N, d) dN + \frac{\Pi V}{kT}. \quad (15)$$

The average concentration of segments in the gap is easily obtained from Eq. (14):

$$\langle \rho \rangle = \int_0^\infty \rho(N, d) N dN, \quad (16)$$

and the number average length of chains in the gap is

$$\langle N \rangle = \frac{\langle \rho \rangle}{\int_0^\infty \rho(N, d) dN}. \quad (17)$$

The segment concentration $\rho(z)$ at coordinate z can be calculated as

$$\rho(z) = \int_0^\infty \rho_0(N) \int_0^N \int_0^{2d} \int_0^{2d} G(z, z_1, n) \times G(z_2, z, N-n) dz_1 dz_2 dn dN. \quad (18)$$

This equation expresses that to find a segment n of a chain of N segments at point z we must have a chain starting from a point z_1 reaching z in n steps, and then continuing for another $N-n$ steps to a point z_2 . The total segment concentra-

tion at point z is then found by integration over all positions z_1 of the starting point and z_2 of the end point, over all segments n , and over all chain lengths N . The factor $\rho_0(N)$ is a normalization factor, ensuring $(1/2d) \int_0^{2d} \rho(z) dz = \langle \rho \rangle$.

The excess amount of segments per unit surface area is defined as

$$\theta^{\text{ex}} = \int_0^d [\rho(z) - \rho_0] dz = d[\langle \rho \rangle - \rho_0]. \quad (19)$$

As discussed in the Introduction, the presence of equilibrium polymers in the gap modifies the interactions between the two surfaces. The force per unit area acting on the plates as a result of the polymers is often called the disjoining pressure. It can be calculated from the grand potential as¹⁸

$$p = -\frac{1}{2A} \left(\frac{\partial \Omega}{\partial d} \right)_{\mu, \Pi, T}. \quad (20)$$

If the polymers cause repulsion between the surfaces p is positive, while p is negative if the polymers cause an attraction between the surfaces.

Because of the exponential chain length distribution $\rho_0(N)$ in the bulk [Eq. (3)], the integrals in Eqs. (15)–(18) can be computed using the Laplace transforms of $G(z, z', N)$ and $Z(N, d)$ with respect to the variable N , defined as

$$\tilde{G}(z, z', s) = \int_0^\infty G(z, z', N) e^{-sN} dN \quad (21)$$

and

$$\begin{aligned} \tilde{Z}(N, s) &= \int_0^\infty Z(N, d) e^{-sN} dN \\ &= \frac{1}{2d} \int_0^{2d} \int_0^{2d} \tilde{G}(z, z', s) dz dz'. \end{aligned} \quad (22)$$

Using this, the integral in Eq. (15) can be written as

$$\int_0^\infty \rho(N, d) dN \equiv \frac{\rho_0}{\langle N_0 \rangle^2} \tilde{Z}(\langle N_0 \rangle^{-1}, d), \quad (23)$$

where we have used Eqs. (14) and (3). Here $\tilde{Z}(\langle N_0 \rangle^{-1}, d)$ is given by Eq. (22) with the Laplace variable s equal to $\langle N_0 \rangle^{-1}$. Hence, the grand potential Ω can be computed exactly by performing a Laplace transform on $Z(N, d)$. Similarly, the average volume fraction [Eq. (16)] can be calculated from the Laplace transform of $Z(N, d)N$, which is equal to the first derivative $-d\tilde{Z}(s, d)/ds$, and the concentration profile $\rho(z)$ [Eq. (18)] can be found from the Laplace transform of the distribution function $G(z, z', N)$ [Eq. (21)] making use of the convolution theorem. The Laplace transform $\tilde{G}(z, z', s)$ of $G(z, z', N)$ can be obtained by solving the Edwards equation in the Laplace domain:

$$\frac{b^2}{6} \frac{\partial^2 \tilde{G}(z, z', s)}{\partial z^2} = s \tilde{G}(z, z', s) - G(z, z', 0), \quad (24)$$

with $G(z, z', 0) = \delta(z - z')$ [Eq. (7)]. The boundary conditions are obtained by performing a Laplace transform on Eq. (8):

TABLE I. Exact and asymptotic expressions for the grand potential, the concentration profile of monomers, the average monomer concentration, the average length, and the disjoining pressure for equilibrium polymers without sticky ends confined between two surfaces.

		Full expression (a)	Wide gap ($D \gg 1$) (b)	Narrow gap ($D \ll 1$)	
				$D \ll -C^{-1}$ (c)	$D_{cr} < D \ll C^{-1} $ (d)
(1.1)	$\frac{\Omega}{\Pi V}$	$\frac{-C \sinh D}{DA_1}$	$\frac{C}{D(C-1)}$	$1 - \frac{D^2}{3}$	$\frac{C}{C-D}$
(1.2)	$\frac{\rho(z)}{\rho_0}$	$(1 + C\psi_1)^2$	$\left(1 - \frac{Ce^{-\xi}}{C-1}\right)^2$	$\xi^2(D - \frac{1}{2}\xi)^2$	$\frac{D^2}{(D-C)^2}$
(1.3)	$\frac{\langle \rho \rangle}{\rho_0}$	$1 + \frac{3A_1 C \sinh D + BC}{2A_1^2 D}$	$1 + \frac{C(2 - \frac{3}{2}C)}{D(1-C)^2}$	$\frac{2D^4}{15}$	$\frac{D^2}{(D-C)^2}$
(1.4)	$\frac{\langle N \rangle}{\langle N_0 \rangle}$	$1 + \frac{A_1 C \sinh D + BC}{2A_1^2 D + 2A_1 C \sinh D}$	$1 + \frac{C(2-C)}{2D(1-C)^2}$	$\frac{2D^2}{5}$	$\frac{D}{D-C}$
(1.5)	$\frac{p}{\Pi}$	$\frac{-C^2}{A_1^2}$	$\frac{-4C^2 e^{-2D}}{(1-C)^2}$	$-1 + D^2$	$\frac{-C^2}{(D-C)^2}$

with $R_0 = b \sqrt{\frac{\langle N_0 \rangle}{6}}$, $C = cR_0 < 1$, $D = \frac{d}{R_0}$, $\xi = \frac{z}{R_0}$, $D_{cr} = \text{atanh } C$

$A_1 = \sinh D - C \cosh D$, $B = \sinh^2 D + CD$, $\psi_1 = \frac{\cosh(\xi - D)}{A_1}$

$$\left[\frac{1}{\tilde{G}} \frac{\partial \tilde{G}}{\partial z} \right]_{z=0} = - \left[\frac{1}{\tilde{G}} \frac{\partial \tilde{G}}{\partial z} \right]_{z=2d} = -c. \tag{25}$$

The solution of this differential equation can be found using standard techniques (but is too long to display here). The Laplace transformed partition function $\tilde{Z}(\langle N_0 \rangle^{-1}, d)$ can then be obtained by integration over z and z' and division by $2d$ [Eq. (22)], and by substitution of $\langle N_0 \rangle^{-1}$ for s . This procedure results in relatively simple, exact expressions for Ω , $\rho(z)$, $\langle \rho \rangle$, $\langle N \rangle$, and p . In Table I, we have listed these exact formulas, together with approximations for wide gaps and for narrow gaps. We will discuss these results in Secs. IV B and IV C.

B. Infinite separation

First, we consider the situation where the surfaces are infinitely far apart ($d \rightarrow \infty$). The concentration profile of monomers at a single surface is given by Eq. (1.2b) in Table I as a function of the dimensionless parameters $\xi = z/R_0$ and $C = cR_0$ with $R_0 = b \sqrt{\langle N_0 \rangle / 6}$ the radius of gyration of a chain of which the chain length equals the number average length in the bulk. For a nonadsorbing surface ($C < 0$) the monomer concentration close to the wall is lower than in the bulk, while for an adsorbing surface ($C > 0$) it is higher. At the adsorption/depletion transition ($C = 0$), the concentration is not affected by the surface. Obviously, far away from the surface, the concentration goes asymptotically to the bulk value ρ_0 .

For the excess amount of monomers at a single surface [Eq. (19)] we find

$$\frac{\theta^{ex}}{\rho_0} = \frac{R_0 C (2 - \frac{3}{2}C)}{(1-C)^2} \quad (\text{if } C < 1). \tag{26}$$

The excess amount is shown in Fig. 2 as a function of C (the full curve). For $C < 0$ the excess amount is negative: there is a depletion layer near the surface with a thickness $\delta \equiv -\theta^{ex}/\rho_0$ which is proportional to the average radius of gyration. For $C \rightarrow -\infty$, Eq. (26) gives $\delta = -\theta^{ex}/\rho_0 = \frac{3}{2}R_0$, which is slightly larger than the depletion layer thickness for ideal monodisperse polymers²⁹ [$\delta = (2/\sqrt{\pi})R$]. With increasing C , the excess amount becomes less negative, and it becomes positive for $C > 0$. When $C \rightarrow 1$, θ^{ex} goes to infinity. Hence, if the temperature is lowered, so that c increases [and R_0 as well, see Eq. (4)], the excess amount diverges continuously at a critical temperature for which $c_{cr} = R_0^{-1}$. It is instructive to compare this behavior to that of monodisperse chains. For monodisperse ideal polymer chains an adsorption transition at $c = 0$ is observed in the limit $N \rightarrow \infty$:^{29,30} the

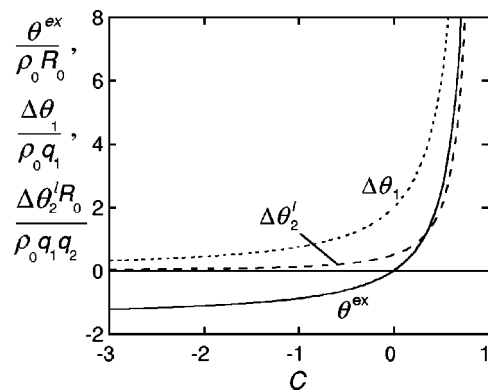


FIG. 2. The behavior of equilibrium polymers at a single surface. Full curve: the excess amount for chains without special adsorbing functional groups (θ^{ex}); dotted curve: extra adsorbed amount of monomers in end-adsorbed chains ($\Delta \theta_1$); dashed curve: extra adsorbed amount of monomers in end-to-end loops ($\Delta \theta_2'$). $\Delta \theta_1$ and $\Delta \theta_2'$ will be discussed in Secs. V B and V C, respectively.

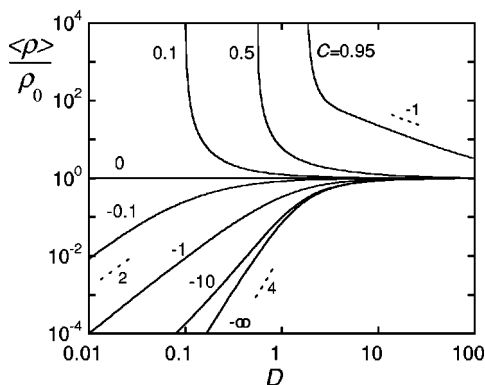


FIG. 3. The average concentration of monomers in the gap (divided by the bulk concentration ρ_0) as a function of the separation distance between the surfaces for several values of C .

excess amount jumps from a negative value to infinity at this point. For finite chains, however, there is a sharp increase in the adsorption at $c=0$, but no transition (the adsorption remains finite). As discussed by Sear,³⁰ the adsorption of polydisperse chains is sensitive to the large N tail of the distribution. If the distribution of chains decays more rapidly with chain length than exponentially (or is cut off at some maximum chain length), the mixture behaves like finite monodisperse chains (no adsorption transition). On the other hand, if the distribution decays more slowly than exponentially there is an adsorption transition at $c=0$ like for infinite monodisperse chains. For the special case of an exponential chain length distribution, like we have for equilibrium polymers [Eq. (3)], the adsorption diverges continuously, rather than via a jump, at a finite value $c_{cr}=R_0^{-1}$ (a second order phase transition). This is clearly seen in Fig. 2 and Eq. (26). It can be concluded that equilibrium polymers behave qualitatively differently from monodisperse polymers of length equal to the average length. Obviously, the ideal chain model is no longer valid in the case of strong adsorption, because excluded volume interactions between adsorbed chains become very important then. Whereas Eq. (1.2b) of Table I predicts the surface concentration $\rho(0)$ to diverge as $1/(1-C)^2$, for real chains the maximum volume fraction of train segments is unity. Nevertheless, we expect that the qualitative differences between the adsorption of equilibrium polymers and that of monodisperse polymers will also be found in more realistic models.

C. Finite separation

For finite separation between the two surfaces, the concentration profile of monomers in the gap is given by Eq. (1.2a) in Table I, and the average monomer concentration is given by Eq. (1.3a). In Fig. 3, $\langle \rho \rangle / \rho_0$ is shown as a function of the reduced half-distance between the surfaces $D = d/R_0$, for several values of C . Obviously for $D \rightarrow \infty$, the concentration in the gap approaches the bulk value. The excess amount per surface is constant for large separations, given by Eq. (26), and the average concentration varies as $|\langle \rho \rangle - \rho_0| \sim D^{-1}$ for $D \gg C^{-1}$ according to Eq. (1.3b). For strong adsorption ($\langle \rho \rangle \gg \rho_0$) this reduces to $\langle \rho \rangle \sim D^{-1}$, which can be seen in Fig. 3 for $C = 0.95$.

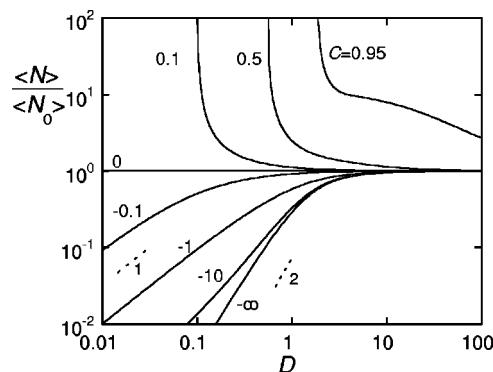


FIG. 4. The average length of chains in the gap as a function of the separation distance between the surfaces for several values of C .

For a nonadsorbing surface ($C < 0$) the monomer concentration close to the surfaces is lower than in the bulk. As the distance between the surfaces decreases, $\langle \rho \rangle$ decreases because it becomes more unfavorable for polymers to be in the gap. The depletion is strongest for $C \rightarrow -\infty$. In this case, our results reduce to those of Schmitt *et al.*,¹⁸ who considered the case of strong repulsion between the segments and the surfaces. For C values less negative, the effect of confinement becomes smaller, and at the adsorption threshold ($C=0$) the average concentration in the gap equals that in the bulk, irrespective of D . At small separations, upon decreasing D the average concentration vanishes proportionally to D^4 if the segment-wall interaction is very unfavorable ($C \ll -D^{-1}$), while closer to the adsorption threshold ($0 < -C \ll D^{-1}$) it vanishes proportionally to D^2 [see Eqs. (1.3c) and (1.3d)].

For an adsorbing surface ($C > 0$), $\langle \rho \rangle$ increases strongly with decreasing surface separation, the more so the larger C . It can be seen from Eq. (1.3a) that the concentration inside the gap diverges when

$$D_{cr} = \operatorname{atanh} C \quad \text{or} \quad C_{cr} = \tanh D. \quad (27)$$

For example, for $C = 0.1$ in Fig. 3, $D_{cr} = \operatorname{atanh} 0.1 \approx 0.1$. At small separations $D < D_{cr}$, the Gaussian chain model predicts an infinite amount of polymer in the gap. Hence, the value of C where the adsorption diverges is unity when the gap is wide, but it is smaller for narrow gaps: 0.95 for $D = 1.47$, 0.5 for $D = 0.55$, and 0.1 for $D = 0.1$. This means that the divergence occurs at a higher temperature in a narrow gap. This phenomenon is analogous to capillary condensation, i.e., the shift of the vapor to liquid phase transition to higher temperatures when the vapor is confined in a narrow slit.

The average length of the chains in the gap as compared to that in the bulk is given by Eq. (1.4a) in Table I. It is shown as a function of D in Fig. 4 for several values of C . Obviously, for an infinite separation distance, the average length equals the bulk value. For nonadsorbing surfaces, the average length is smaller than in the bulk, because the large chains are excluded from the gap. Upon decreasing D the average length decreases. This decrease is at small separations ($D \ll 1$) proportional to D^2 if $C \ll -D^{-1}$ [Eq. (1.4c)] and proportional to D if $0 < -C \ll D^{-1}$ [Eq. (1.4d)]. For C

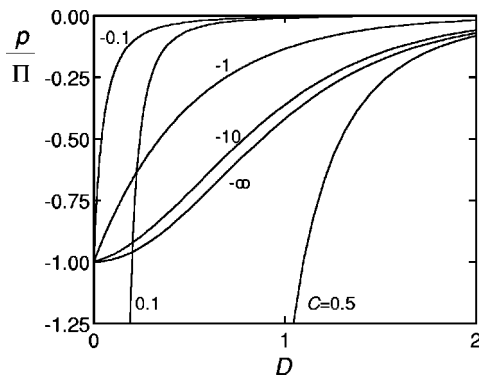


FIG. 5. The disjoining pressure between the plates (divided by the bulk osmotic pressure Π) as a function of the separation distance for several values of C .

$=0$ the average length is equal to that in the bulk, irrespective of D . For adsorbing surfaces ($C > 0$) $\langle N \rangle$ is larger than in the bulk, because large chains are preferentially adsorbed. It increases strongly as D decreases and diverges at $D = D_{cr}$, like the average concentration in the gap.

The disjoining pressure p due to the equilibrium polymers is given by Eq. (1.5a) in Table I. It is shown in Fig. 5 as a function of D for several values of C . As we can see, the two surfaces attract each other for all $C \neq 0$, both for adsorption ($C > 0$) and for depletion ($C < 0$). Only for $C = 0$ the interaction is zero. For $C < 0$ the attraction is due to the depletion mechanism. For small separations the depletion layers of the two surfaces overlap and the monomer concentration in the middle of the gap is lower than that in the bulk. As a result the osmotic pressure of the bulk Π is not balanced by the pressure inside the gap, and the two surfaces are pushed together. At very small separations almost all polymer is depleted from the gap and the osmotic pressure inside the gap vanishes. The effective pressure pushing the surfaces together in this case is equal to Π , which follows also immediately from Eqs. (15) and (20) with $\rho(N, d) = 0$ for all N . The range of the attraction depends on the value of C . It is of order R_0 for $C = -\infty$. For this case Eq. (1.4a) reduces to $p/\Pi = -1/\cosh^2 D$, which is also the expression given by Schmitt *et al.*¹⁸ For C less negative, the range becomes smaller, because the distance over which the polymer solution is perturbed by the surfaces is reduced.

For $C > 0$ the attraction is a result of the formation of bridges between the surfaces [Fig. 1(A),e]. This effect is much stronger than the depletion attraction, and becomes infinitely strong when the adsorbed amount diverges, i.e., as $D \rightarrow D_{cr}$.

Just like ordinary homopolymers under equilibrium conditions, equilibrium polymers without adsorbing end groups always induce an attraction between two surfaces. In the next section we investigate the effect of specific adsorption of the end groups of the chains.

V. END-ADSORBING EQUILIBRIUM POLYMERS

A. Statistical thermodynamics

At both ends of an equilibrium polymer, there is a free (unlinked) functional group. In the case of nondirectional

monomers with self-complementary bonding groups, both ends are identical. If the monomers are directional, there is an acceptor group at one end, and a complementary donor group at the other end. The functional groups will generally have a different interaction with the surface than the segments in the interior of the chain, for example, because they can form hydrogen bonds with groups on the surface. In this section we consider the effect of equilibrium polymers of which one or both functional groups have a specific interaction with the surfaces (i.e., polymers with one or two sticky ends). Chains with one sticky end group tend to adsorb with one end on the surface [Fig. 1(B),f]. Chains with two sticky ends can also form end-to-end loop conformations and end-to-end bridge conformations [see (g) and (h) of Fig. 1(C)].

If the functional groups of the chains have a specific interaction with the surface, conformations with the sticky end at the surface will have a higher probability. The statistical weight of these conformations can be found by multiplication of the corresponding distribution function $G(z, z', N)$ by a Boltzmann factor $e^{-\epsilon_1/kT}$, where ϵ_1 is the difference between the adsorption energy of the sticky end and that of the other segments in the chain. The partition function of an end-adsorbed chain [Fig. 1(f)], i.e., a chain of which the first segment is adsorbed (at $z=0$) and the last segment can be anywhere, thus becomes [analogously to Eq. (13)]

$$\begin{aligned} \Delta Z_1(N, d) &= \frac{e^{-\epsilon_1/kT} - 1}{2d} \int_0^{2d} \int_0^\delta G(z, z', N) dz dz' \\ &\approx \frac{q_1}{2d} \int_0^{2d} G(z, 0, N) dz, \end{aligned} \quad (28)$$

where δ is the effective distance over which the sticky end-segment interacts with the surface, and where $q_1 = \delta(e^{-\epsilon_1/kT} - 1)$. The term -1 in the numerator of the factor before the integral in Eq. (28) is added to subtract the contribution of conformations with the end on the surface that is already included in Z [Eq. (13)]. Hence, ΔZ_1 is a measure for the *additional* end-adsorbed chains as a result of the specific interaction of the functional group with the surface. The second equality in (28) is valid for $\delta \ll d$. For chains of which only one functional group has a special interaction with the surface, Eq. (28) is the only additional contribution. If both functional groups adsorb preferentially, however, there is a similar contribution of end-adsorbed chains with the last segment adsorbed and the first segment free. Moreover, end-to-end loops and end-to-end bridges become important [see (g) and (h) of Fig. 1(C)]. For an end-to-end loop (with both ends at $z=0$) the partition function is

$$\begin{aligned} \Delta Z_2^l(N, d) &= \frac{(e^{-\epsilon_1/kT} - 1)(e^{-\epsilon_2/kT} - 1)}{2d} \\ &\quad \times \int_0^\delta \int_0^\delta G(z, z', N) dz dz' \\ &\approx \frac{q_1 q_2}{2d} G(0, 0, N), \end{aligned} \quad (29)$$

TABLE II. Exact and asymptotic expressions for the excess number of end-adsorbed chains per unit area, their contribution to the concentration profile, the number of monomers per unit area in end-adsorbed chains, their average length, and their contribution to the disjoining pressure for chains with only one sticky end. The two surfaces are considered to be identical.

		Full expression (a)	Wide gap ($D \gg 1$) (b)	Narrow gap ($D \ll 1$)	
				$D \ll -C^{-1}$ (c)	$D_{cr} < D \ll C^{-1} $ (d)
(2.1)	$\frac{\Delta\sigma_1 \langle N_0 \rangle}{q_1 \rho_0}$	$\frac{\sinh D}{A_1}$	$\frac{1}{1-C}$	$\frac{-D(3-D^2)}{3C}$	$\frac{D}{D-C}$
(2.2)	$\frac{\Delta\rho_1(z)}{Q_1 \rho_0}$	$\psi_1(1+C\psi_1)$	$\frac{e^{-\zeta} + Ce^{-2\zeta}}{1-C + (1-C)^2}$	$\frac{\zeta(\zeta-2D)}{2C}$	$\frac{D}{(D-C)^2}$
(2.3)	$\frac{\Delta\theta_1}{q_1 \rho_0}$	$\frac{B+A_1 \sinh D}{2A_1^2}$	$\frac{(2-C)}{2(1-C)^2}$	$\frac{D^3}{-3C}$	$\frac{D^2}{(D-C)^2}$
(2.4)	$\frac{\langle N_1 \rangle}{\langle N_0 \rangle}$	$\frac{1}{2} + \frac{B}{2A_1 \sinh D}$	$\frac{2-C}{2(1-C)}$	$\frac{D^2}{3}$	$\frac{D}{D-C}$
(2.5)	$\frac{\Delta p_1}{Q_1 \Pi}$	$\frac{-C}{A_1^2}$	$\frac{-4Ce^{-2D}}{(1-C)^2}$	$\frac{(1-D^2)}{-C}$	$\frac{-C}{(D-C)^2}$

with $R_0 = b \sqrt{\frac{\langle N_0 \rangle}{6}}$, $C = cR_0 < 1$, $D = \frac{d}{R_0}$, $\zeta = \frac{z}{R_0}$, $Q_1 = \frac{q_1}{R_0}$

$A_1 = \sinh D - C \cosh D$, $B = \sinh^2 D + CD$, $\psi_1 = \frac{\cosh(\zeta - D)}{A_1}$, $D_{cr} = \operatorname{atanh} C$

where q_1 and q_2 account for the binding energies of the two functional groups at either end. For nondirectional chains with two identical end groups, $q_1 = q_2$. For directional chains, q_1 and q_2 may be different. The partition function of an end-to-end bridge (with the first segment at $z = 0$ and the last segment at $z = 2d$) is

$$\begin{aligned} \Delta Z_2^b(N, d) &= \frac{(e^{-\epsilon_1/kT} - 1)(e^{-\epsilon_2/kT} - 1)}{2d} \\ &\times \int_0^\delta \int_{2d-\delta}^{2d} G(z, z', N) dz dz' \\ &\approx \frac{q_1 q_2}{2d} G(0, 2d, N). \end{aligned} \tag{30}$$

The substitution of Eqs. (28)–(30) in Eq. (14) gives the additional number of chains of length N per unit volume belonging to a class of conformations i (denoting chains with one adsorbed end, end-to-end loops, or end-to-end bridges):

$$\Delta\rho_i(N, d) = 2\Delta Z_i(N, d)\rho_0(N), \tag{31}$$

where the factor 2 accounts for the two surfaces: since the two surfaces are identical, there are as many end-adsorbed chains on the surface at $z = 0$ as on the surface at $z = 2d$. The extra amount of monomers *per unit surface area* in chains belonging to a class of conformations i can be calculated as

$$\Delta\theta_i = d \int_0^\infty \Delta\rho_i(N, d) N dN, \tag{32}$$

and the additional number of chains in an i conformation per unit area is

$$\Delta\sigma_i = d \int_0^\infty \Delta\rho_i(N, d) dN. \tag{33}$$

The average length can be calculated as $\langle N_i \rangle = \Delta\theta_i / \Delta\sigma_i$.

From Eq. (15) it follows that the contributions to the grand potential of chains in the various conformations are additive. Chains in conformation i contribute an additional amount $\Delta\Omega_i/kT = -2A\Delta\sigma_i$ to the grand potential, and their contribution to the disjoining pressure is [see Eq. (20)] $\Delta p_i = -(1/2A)(\partial\Delta\Omega_i/\partial d)_{\mu, \Pi, T}$. The concentration profile of monomers in end-adsorbed chains can be found by modifying Eq. (18), restricting the integration over the position of the starting point z_1 to the region $0 \leq z \leq \delta$. For end-to-end loops and bridges, also the position of the end point z_2 is restricted.

In our treatment of chains with sticky ends, we have assumed that the amount of end-adsorbed chains is determined by the adsorption energy ϵ of the end segments. One can also imagine a situation where the end groups of the chain bind strongly to specific groups on the surface. If this binding is strong and the number of binding sites on the surface is limited, then the amount of end-adsorbed chains is determined by the concentration of active groups on the surface rather than by the adsorption energy. In this case, we must have $\Delta\sigma_1 + 2\Delta\sigma_2^l + \Delta\sigma_2^b = \sigma$, with σ the number of active groups per unit area. The parameter ϵ may then be considered as a Lagrange multiplier for the amount of surface groups.

B. Equilibrium polymers with one adsorbing end

In this section we consider directional chains of which only one functional group adsorbs preferentially on the surfaces, i.e., $q_1 > 0$ and $q_2 = 0$ [Fig. 1(B)]. Exact expressions can again be obtained using the Laplace transform of $G(z, 0, N)$, Eq. (21). These are given in Table II, as well as limiting expressions for wide and narrow gaps. First we con-

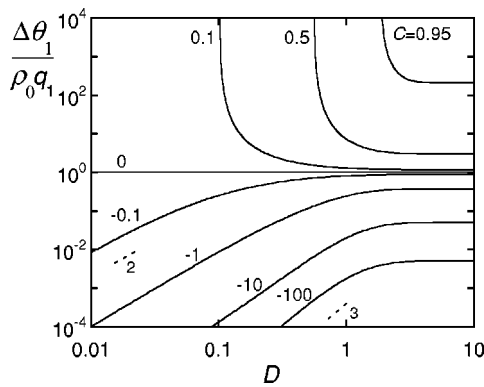


FIG. 6. The amount of monomers per unit area in end-adsorbed chains (divided by $\rho_0 q_1$) as a function of the separation distance for several values of C .

consider again the situation where the two surfaces are at infinite separation ($d \rightarrow \infty$). The concentration profile of end-adsorbed chains at a single surface is given by Eq. (2.2b) in Table II. It is a sum of two exponential decays. For $z \gg R_0$ the first term in Eq. (2.2b) dominates and the concentration of end-adsorbed chains decays exponentially to zero with a decay length equal to R_0 . For a surface which is adsorbing for the main-chain segments ($C > 0$) both terms have the same sign and the profile is monotonic. For a surface which is nonadsorbing for the main-chain segments ($C < 0$) on the other hand, the two terms have opposite signs and the profile is nonmonotonic with a maximum at a distance $z = R_0 \ln(2C/(C-1))$ from the surface. The chains then avoid the region close to the surface because of entropic restrictions. At the adsorption threshold for the main-chain segments ($C = 0$) the second term in Eq. (2.2b) vanishes and the profile reduces to a simple exponential decay.

The additional amount of monomers per unit area in end-adsorbed chains at a single surface is given in Eq. (2.3b), and is plotted in Fig. 2 (the dotted curve). Obviously, $\Delta\theta_1$ is proportional to q_1 . For $C \rightarrow -\infty$, $\Delta\theta_1$ goes to zero (for constant q_1). It increases with increasing C and it diverges if C approaches unity, just like the excess amount for chains without sticky ends described in Sec. IV B. The total excess amount θ_i^{ex} for chains with one sticky end is the sum of the contributions of chains with both ends free θ^{ex} and that of the end-adsorbed chains $\Delta\theta_1$. For a single surface this becomes [with Eqs. (26) and (2.3b)]

$$\frac{\theta_i^{\text{ex}}}{\rho_0 R_0} = \frac{C(4-3C) + Q_1(2-C)}{2(1-C)^2} \quad (\text{if } C < 1), \quad (34)$$

where $Q_1 = q_1/R_0$. The first term in the numerator originates from the free chains and the second term from the end-adsorbed chains. It can be seen that the contribution of the end-adsorbed chains becomes significant when Q_1 is of the same order of magnitude as C , and it dominates for $Q_1 \gg C$.

The average length of the end-adsorbed chains on a single surface is given by Eq. (2.4b). For $C \rightarrow -\infty$, $\langle N_1 \rangle = \frac{1}{2}\langle N_0 \rangle$. It increases with increasing C , for $C = 0$, $\langle N_1 \rangle = \langle N_0 \rangle$, and for $C > 0$, $\langle N_1 \rangle > N_0$. For $C = 1$, the average length diverges, like the adsorbed amount.

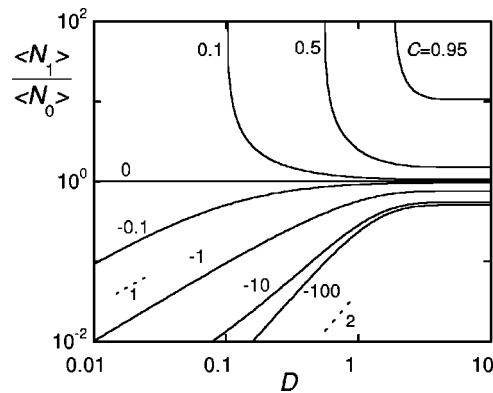


FIG. 7. The average length of chains with one adsorbed end as a function of the separation distance for several values of C .

Figure 6 shows the additional amount of monomers in end-adsorbed chains $\Delta\theta_1$ [given by Eq. (2.3a)] as a function of the distance between the surfaces. When the main-chain segments do not adsorb ($C < 0$), $\Delta\theta_1$ decreases as the distance between the surfaces decreases. At small separations, upon decreasing D the amount of monomers in end-adsorbed chains decreases proportionally to D^3 for $C \ll -D^{-1}$ [Eq. (2.3c)], and proportionally to D^2 for $0 < -C \ll D^{-1}$ [Eq. (2.3d)]. When the main-chain segments do adsorb ($C > 0$), $\Delta\theta_1$ increases strongly with decreasing D , and it diverges at $D = D_{\text{cr}}$ [given by Eq. (27)], like the average concentration of chains without sticky ends (see Sec. IV C).

The average length of end-adsorbed chains [Eq. (2.4a)] is shown in Fig. 7. For $C < 0$ it decreases when the surface separation decreases, because the presence of the second surface hinders the growth of the end-adsorbed chain. At small separations, upon decreasing D it decreases proportionally to D^2 for $C \ll -D^{-1}$, and proportionally to D for $0 < -C \ll D^{-1}$. For $C > 0$ the average length increases and diverges for $D = D_{\text{cr}}$, like the adsorbed amount.

The contribution of the end-adsorbed chains to the disjoining pressure is given by Eq. (2.5a). It is plotted in Fig. 8. For equilibrium polymers of which the main-chain segments do not adsorb ($C < 0$), the interaction is repulsive. The strength of the repulsion at small separations increases as C becomes less negative (for constant $Q_1 = q_1/R_0$), because the number of end-adsorbed chains is larger if C is not too much below the adsorption threshold (see Fig. 6). At larger

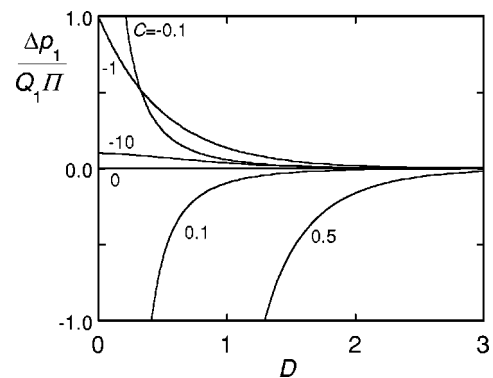


FIG. 8. The contribution of end-adsorbed chains to the disjoining pressure for several values of C .

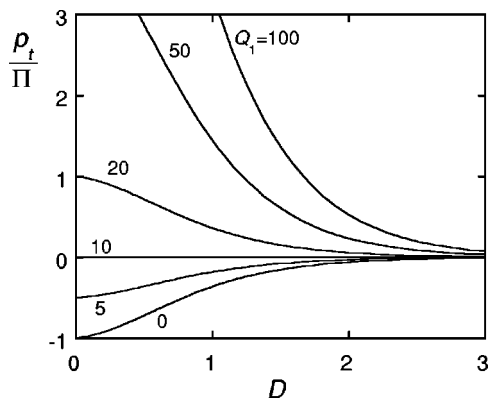


FIG. 9. The total disjoining pressure for directional chains with one sticky end for several values of Q_1 , and $C = -10$.

separations, however, the value of Δp_1 is a nonmonotonic function of C , as can be seen from Eq. (2.5b). Therefore, the curves in Fig. 8 intersect for $C < 0$. For $C = 0$ the disjoining pressure due to the end-adsorbed chains vanishes (in this case the end-adsorbed chains are not affected by the other surface, which acts as a reflecting boundary). Equilibrium polymers of which the main-chain segments do adsorb ($C > 0$), in contrast, cause an attraction between the surfaces, because the chain can adsorb on the other surface [and form a bridge; see (e) of Fig. 1(B)]. The bridging attraction becomes very large if D approaches D_{cr} .

The total disjoining pressure for chains with one sticky end is the sum of the contributions p of the chains with both ends free [Eq. (1.5a)] and Δp_1 of the end-adsorbed chains [Eq. (2.5a)]:

$$\frac{p_t}{\Pi} = \frac{p + \Delta p_1}{\Pi} = \frac{-C^2 - Q_1 C}{[\sinh D - C \cosh D]^2} \quad (\text{if } C < C_{cr}). \quad (35)$$

The contribution of the end-adsorbed chains obviously becomes more important if the ends adsorb more strongly (i.e., for larger Q_1 or ϵ_1). In Fig. 9 we have shown the total disjoining pressure for chains with one sticky end as a function of the separation distance D for $C = -10$, and several values of Q_1 . Obviously, for $Q_1 = 0$ (or $\epsilon_1 = 0$), there is no extra contribution of the end-adsorbed chains and the force for this value of C is attractive due to the depletion of chains from the gap (the same as in Fig. 5). If the adsorption energy of the end-segment increases, the attraction between the surfaces becomes weaker due to the repulsive contribution of the end-adsorbed chains (see Fig. 8). For $Q_1 = -C$ the depletion attraction and the steric repulsion due to the end-adsorbed chains just compensate each other, and the net interaction is zero. For strong end-adsorption, $Q_1 > -C$, the repulsive force Δp_1 dominates and the surfaces repel each other. Plots for other values of $C < 0$ look similar, while for $C > 0$ the force is always attractive because both the chains with free ends and the end-adsorbed chains give an attractive contribution in this case.

C. Equilibrium polymers with two adsorbing ends

Equilibrium polymers of which both functional groups have a specific interaction with the surface can form, besides

end-adsorbed chains, also end-to-end loops and end-to-end bridges [see (g) and (h) of Fig. 1(C)]. Obviously, bridges can only be formed if the surfaces are not too far apart. Expressions for the adsorbed amounts, the average lengths, the concentration profile, and the contributions to the disjoining pressure for end-to-end loops and end-to-end bridges are given in Table III. First, we consider again a single surface ($d \rightarrow \infty$), for which there are no bridges. The concentration profile of end-to-end loops on a single surface is given by Eq. (3.2b) in Table III. For all C , the concentration of segments belonging to end-to-end loops decays exponentially to zero with a decay length $R_0/2$.

The additional amount of end-to-end loops on a single surface, given by Eq. (3.3b), is shown in Fig. 2 (the dashed curve). Obviously, $\Delta \theta_2^l$ is proportional to $q_1 q_2$. For $C \rightarrow -\infty$, $\Delta \theta_2^l$ goes to zero. It increases with increasing C and it diverges if C approaches unity, like the adsorbed amounts of chains without sticky ends and end-adsorbed chains described in Secs. IV B and V B. The total excess amount θ_t^{ex} for chains with two sticky ends is the sum of the contributions of chains with both ends free θ^{ex} , of the chains with one adsorbed end $\Delta \theta_1$, and of the chains with two adsorbed ends $\Delta \theta_2$. For a single surface this becomes [with Eqs. (26), (2.3b), and (3.3b)]

$$\frac{\theta_t^{\text{ex}}}{\rho_0 R_0} = \frac{C(4 - 3C) + (Q_1 + Q_2)(2 - C) + Q_1 Q_2}{2(1 - C)^2} \quad (\text{if } C < 1). \quad (36)$$

The first term in the numerator comes from the free chains, the second term from the chains with one of their ends adsorbed, and the last term from the end-to-end loops.

The average length of the end-to-end loops on an isolated surface is given by Eq. (3.4b). For $C < 0$, large loops are unlikely, and the average size of a loop is small. If $C > 0$, the size of the loops becomes larger and it diverges for $C = 1$ just like the adsorbed amount. It can be seen that the average size of end-to-end loops is smaller than that of chains with only one adsorbed end [Eq. (2.4b)] by a factor $2 - C$. This is because the probability that a chain starting from the surface comes back to the surface to make a loop is smaller if the chain is longer, the more so the more negative C .

As the distance between the surfaces decreases the extra amount of end-to-end loops on the surface changes, and also end-to-end bridges are being formed. Figure 10 shows the adsorbed amounts of end-to-end loops [full curves, Eq. (3.3a)] and end-to-end bridges [dashed curves, Eq. (3.8a)] as a function of the separation distance. Obviously, for large separations the amount of end-to-end loops goes to a constant value, while the amount of bridges goes to zero.

For $C > 0$, the number of loops increases with decreasing separation, and diverges as $D \rightarrow D_{cr}$, like for chains without adsorbing ends (Sec. IV C) and for chains with one adsorbed end (Sec. V B). For $C < 0$ on the other hand, the variation of the amount of end-to-end loops is more complicated. For $C \leq -1$, the amount of monomers in end-to-end loops decreases monotonically as the surface separation becomes smaller, because the presence of the second surface hinders

TABLE III. Exact and asymptotic expressions for the excess number of end-to-end loops and bridges per unit area, their contribution to the concentration profile, the number of monomers per unit area in end-to-end loops and bridges, their average length, and their contribution to the disjoining pressure. The two surfaces are considered to be identical.

		Full expression (a)	Wide gap ($D \gg 1$) (b)	Narrow gap ($D \ll 1$)	
				$D \ll -C^{-1}$ (c)	$D_{cr} < D \ll C^{-1} $ (d)
(3.1)	$\frac{\Delta\sigma_2^l \langle N_0 \rangle}{q_1 Q_2 \rho_0}$	$\frac{\cosh D}{2A_1} + \frac{\sinh D}{2A_2}$	$\frac{1}{1-C}$	$\frac{1-2CD}{2C^2 D}$	$\frac{1}{2(D-C)}$
(3.2)	$\frac{\Delta\rho_2^l(z)}{Q_1 Q_2 \rho_0}$	$\frac{1}{2}(\psi_1^2 + \psi_2^2)$	$\frac{e^{-2\zeta}}{(1-C)^2}$	$\frac{D^2 + (D-\zeta)^2}{2C^2 D^2}$	$\frac{1}{2(D-C)^2}$
(3.3)	$\frac{\Delta\theta_2^l}{q_1 Q_2 \rho_0}$	$\frac{y_1 A_1^2 + y_2 A_2^2}{8A_1^2 A_2^2}$	$\frac{1}{2(1-C)^2}$	$\frac{2D}{3C^2}$	$\frac{D}{2(D-C)^2}$
(3.4)	$\frac{\langle N_2^l \rangle}{\langle N_0 \rangle}$	$\frac{y_1 A_1^2 + y_2 A_2^2}{4A_1 A_2 A_3}$	$\frac{1}{2(1-C)}$	$\frac{2D}{-3C}$	$\frac{D}{D-C}$
(3.5)	$\frac{\Delta p_2^l}{Q_1 Q_2 \Pi}$	$\frac{A_1^2 - A_2^2}{2A_1^2 A_2^2}$	$\frac{2(C+1)e^{-4D}}{(C-1)^3}$	$\frac{1 - \frac{4}{3}D^2 + \frac{16}{15}D^4}{2C^2 D^2}$	$\frac{-1}{2(D-C)^2}$
(3.6)	$\frac{\Delta\sigma_2^b \langle N_0 \rangle}{q_1 Q_2 \rho_0}$	$\frac{1}{2A_1 A_2}$	$\frac{2e^{-2D}}{(1-C)^2}$	$\frac{1}{2C^2 D}$	$\frac{1}{2(D-C)}$
(3.7)	$\frac{\Delta\rho_2^b(z)}{Q_1 Q_2 \rho_0}$	$\frac{1}{2}(\psi_1^2 - \psi_2^2)$	$\frac{2e^{-2D}}{(1-C)^2}$	$\frac{\zeta(2D-\zeta)}{2C^2 D^2}$	$\frac{1}{2(D-C)^2}$
(3.8)	$\frac{\Delta\theta_2^b}{q_1 Q_2 \rho_0}$	$\frac{y_2 A_2^2 - y_1 A_1^2}{8A_1^2 A_2^2}$	$\frac{2De^{-2D}}{(1-C)^2}$	$\frac{2D}{3C^2}$	$\frac{D}{2(D-C)^2}$
(3.9)	$\frac{\langle N_2^b \rangle}{\langle N_0 \rangle}$	$\frac{y_2 A_2^2 - y_1 A_1^2}{4A_1 A_2}$	D	$\frac{2D}{-3C}$	$\frac{D}{D-C}$
(3.10)	$\frac{\Delta p_2^b}{Q_1 Q_2 \Pi}$	$-\frac{(A_1^2 + A_2^2)}{2A_1^2 A_2^2}$	$-\frac{4e^{-2D}}{(1-C)^2}$	$-\frac{1 - \frac{2}{3}D^2 + \frac{14}{15}D^4}{2C^2 D^2}$	$\frac{-1}{2(D-C)^2}$

with $R_0 = b \sqrt{\frac{\langle N_0 \rangle}{6}}$, $C = cR_0 < 1$, $D = \frac{d}{R_0}$, $\zeta = \frac{z}{R_0}$, $Q_1 = \frac{q_1}{R_0}$, $Q_2 = \frac{q_2}{R_0}$, $D_{cr} = \text{atanh } C$

$A_1 = \sinh D - C \cosh D$, $A_2 = \cosh D - C \sinh D$, $y_1 = \sinh 2D - 2D$, $y_2 = \sinh 2D + 2D$

$A_3 = \sinh 2D - C \cosh 2D$, $\psi_1 = \frac{\cosh(\zeta - D)}{A_1}$, $\psi_2 = \frac{\sinh(\zeta - D)}{A_2}$

the formation of large loops. For $-1 < C < 0$, however, the amount of end-to-end loops first increases as the surfaces come closer together and then it decreases for small separations. At the critical value ($C=0$), the amount of end-to-end loops increases monotonically with decreasing surface separation.

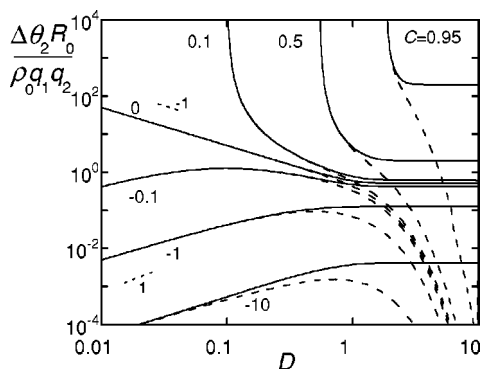


FIG. 10. The amount of monomers per unit area in end-to-end loops (full curves) and end-to-end bridges (dashed curves) (both divided by $\rho_0 q_1 Q_2$) as a function of the separation distance for several values of C .

Hence, unlike for chains without adsorbing end segments or end-adsorbed chains, for end-to-end loops the adsorbed amount depends on R_0 and d at critical conditions ($C=0$). This behavior is quite similar to that of cyclic polymers, for which the average concentration in a gap at critical conditions also increases as the gap becomes narrower.²³ The latter behavior was explained by the difference in conformational entropy between an open chain and a ring. The entropy loss of a ring close to the surface is smaller than that of an open chain of the same size. This difference is quite small, so that it is unimportant when one of the two effects of the surface on the chain (entropy loss or adsorption energy) dominates, but it becomes important close to the critical conditions: when $C=0$ the entropy loss and the energy gain of a ring polymer do not completely compensate each other like for an open chain, and ring polymers are attracted to the surface.²³ This effect was called a net attraction between the segments and surface of a topological origin.²³ Here, we find a similar behavior for loops. For $-1 < C < 0$, the curves are nonmonotonic. At large surface separations the adsorbed amount increases upon decreasing the surface separation as a

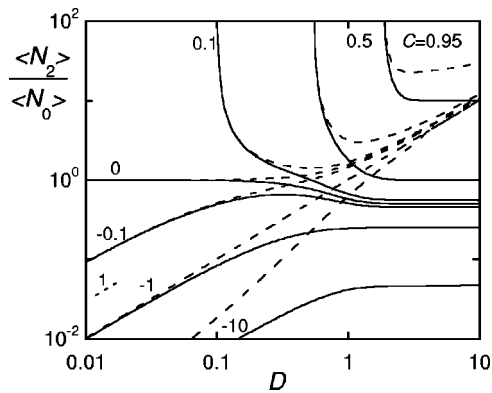


FIG. 11. The average length of the end-to-end loops (full curves) and end-to-end bridges (dashed curves) as a function of the separation distance for several values of C .

result of the topological attractions. At smaller distances the loss of conformational entropy starts to dominate and loops are excluded from the gap. At intermediate distance, $\Delta\theta_2^l$ passes through a maximum, which shifts to smaller values of D as C approaches zero.

The dashed curves in Fig. 10 represent the end-to-end bridges. At large separations $D \gg 1$, the amount of bridges is obviously very low [Eq. (3.8b)]. When the distance between the surfaces becomes of the order of the average radius of gyration, bridges are being formed. For an adsorbing surface, the amount of end-to-end bridges increases monotonically with decreasing surface separation. For a nonadsorbing surface, on the other hand, $\Delta\theta_2^b$ passes through a maximum. The number of end-to-end bridges per unit area [$\Delta\sigma_2^b$, Eq. (3.6a)] increases monotonically with decreasing surface separation, but at the same time the average length of the bridges becomes smaller as the surfaces come closer together [see also Fig. 11 and Eq. (3.9a)]. As a result, $\Delta\theta_2^b = \Delta\sigma_2^b \langle N_2^b \rangle$ passes through a maximum. At very small separations ($D \ll 1$) loops and bridges have the same contribution to the excess amount ($\Delta\theta_2^l \approx \Delta\theta_2^b$) [see Eqs. (3.3c), (3.3d) and (3.8c), (3.8d)]. Physically, this means that a random walk starting from one surface can turn back to the first surface or continue towards the other surface with equal probabilities if the surfaces are very close together. At the critical condition $C = 0$, both $\Delta\theta_2^l$ and $\Delta\theta_2^b$ are proportional to D^{-1} at small separations. For a nonadsorbing surface ($C < 0$) both decrease proportionally to D upon decreasing D .

Figure 11 shows the average size of the end-to-end loops [full curves, Eq. (3.4a)] and end-to-end bridges [dashed curves, Eq. (3.9a)] as a function of the separation distance between the surfaces. For an adsorbing surface the average size of the end-to-end loops increases with decreasing separation. For a nonadsorbing surface with $C < -1$, on the other hand, it decreases monotonically. For $-1 < C < 0$ the average length passes through a maximum. The origin of this maximum is the same as that of the maximum in the adsorbed amount. The average size of the end-to-end bridges at large surface separations increases proportionally to D with increasing distance, because a bridge needs to have at least a length $2d$. At small separations the average length of the loops and bridges are approximately equal [see Eqs. (3.4c),

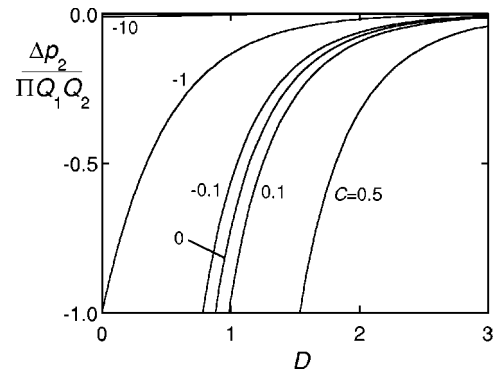


FIG. 12. The contribution of chains with two adsorbed ends (end-to-end loops and bridges) to the disjoining pressure for several values of C .

(3.4d) and (3.9c), (3.9d)], like the adsorbed amounts. At the critical value $C = 0$ the average length of loops and bridges in a narrow gap becomes equal to the average length of a chain in the bulk. For $C < 0$ the average length decreases proportionally to D upon decreasing D for small separations. The average size becomes of the order of one or a few Kuhn segments for nonadsorbing surfaces at small separations. Obviously, for this case the Gaussian chain approximation is no longer valid, and the results become inaccurate. We note furthermore that for the special case that $C = -1$, the average length of the bridges reduces to $\langle N_2^b \rangle / \langle N_0 \rangle = D$ for all D .

The contributions of end-to-end loops and bridges to the disjoining pressure are given by Eqs. (3.5a) and (3.10a), respectively. The contribution of the end-to-end bridges is attractive for all C , whereas the contribution of the end-to-end loops is repulsive for $C < -1$ and attractive for $C > -1$. For $C = -1$ the contribution of the loops to the disjoining pressure vanishes. The total contribution of loops and bridges $\Delta p_2 = \Delta p_2^l + \Delta p_2^b$ is plotted as a function of D for several values of C in Fig. 12. The force is attractive for all C . Hence, the attractive force due to the bridges is more important than the repulsive force due to the loops. For $C \ll -1$ the attraction is rather weak, because the contributions of the loops and bridges almost cancel. As C becomes less negative, the attraction due to the bridges increases strongly, because the amount of bridges increases. At the same time the force due to the loops becomes less repulsive. For $C > -1$, the force due to the loops becomes attractive, too, as a result of the topological attraction between segments of loops and the surface near the critical conditions. In this regime the total interaction becomes strongly attractive.

The total interaction between the two surfaces in the presence of equilibrium polymers with two sticky ends is the sum of the contributions of chains with no, one, and two adsorbed ends:

$$\begin{aligned} \frac{p_t}{\Pi} &= \frac{p + \Delta p_1 + \Delta p_2^l + \Delta p_2^b}{\Pi} \\ &= \frac{-C^2 - C(Q_1 + Q_2) - Q_1 Q_2}{(\sinh D - C \cosh D)^2} \\ &\quad (\text{if } C < C_{\text{cr}}). \end{aligned} \quad (37)$$

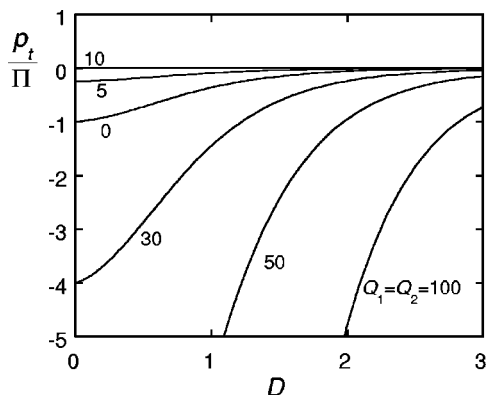


FIG. 13. The total disjoining pressure for chains with two sticky end groups for several values of $Q_1 = Q_2$, and $C = -10$.

Here Δp_1 contains a contribution of chains with the first segment adsorbed (containing a factor Q_1) and chains with the last segment adsorbed (containing a factor Q_2). The total disjoining pressure due to chains with two sticky ends (with $Q_1 = Q_2$) is shown in Fig. 13 for several values of the adsorption energy of the end-groups and for $C = -10$. For $Q_1 = Q_2 = 0$, the ends do not adsorb preferentially, and the force is attractive due to the depletion of chains from the gap (see Fig. 5). For values of $Q_1 = Q_2 < -C$, the force becomes less attractive upon increasing $Q_1 = Q_2$, because more and more chains adsorb with one end on the surface, giving rise to a steric repulsion. It can be seen from Eq. (37) that for $Q_1 = Q_2 = -C$ the total force is zero, because the attractive and repulsive contributions just cancel. For $Q_1 = Q_2 > -C$, the attraction becomes stronger again as a result of the formation of end-to-end bridges. Hence, for $Q_1 = Q_2$ the total disjoining pressure is always negative (attractive), except for $Q_1 = Q_2 = -C$, for which the net force is zero. If $Q_1 \neq Q_2$, the force can be either attractive or repulsive, but it is always a monotonic function of D .

VI. CONCLUDING REMARKS

In this paper we have considered the behavior of ideal equilibrium polymers (without excluded volume) confined between two flat surfaces, and their effect on the forces between two surfaces. The equilibrium polymers were allowed to adsorb on the surfaces or be repelled by them, and specific adsorption interactions between the functional end groups and the surface were considered. As a result of the exponential chain length distribution in the bulk solution, we could make use of the properties of Laplace transforms to obtain exact analytical expressions for the concentration profile, the adsorbed amount, the average length, and the contribution to the disjoining pressure of the confined equilibrium polymers.

The adsorption behavior of equilibrium polymers is qualitatively different from that of monodisperse chains: with increasing adsorption energy (or decreasing temperature) the adsorbed amount diverges continuously at a certain value of the adsorption energy which depends on the average size of the polymer chains. At the same time the average length of the chains diverges. When the chains are confined

between two surfaces, this transition shifts to lower values of the adsorption energy (or higher temperatures).

The effect of equilibrium polymers on the force between two surfaces is always attractive if the functional groups of the monomers do not bind specifically at the surfaces. For nonadsorbing surfaces this force is a depletion force which is determined by the osmotic pressure of the solution. For adsorbing surfaces there is a bridging attraction.

When one of the functional groups of a monomer binds to the surface, the attraction becomes weaker due to steric repulsion and it becomes repulsive if the end adsorption is strong (as long as the main-chain segments do not adsorb on the surface). When both ends adsorb on the surface, end-to-end loops and bridges can be formed. If the main-chain segments do not adsorb, loops give a repulsive contribution to the force, and bridges an attractive contribution. The net force for equilibrium polymers with two sticky ends is always attractive if both ends are identical. The strength of the attraction first decreases and then increases as the end groups bind more strongly to the surface. In this paper we have only considered preferential adsorption of the end segments. All formulas derived in Sec. V, however, also apply to equilibrium polymers of which the end groups are more strongly repelled by the surfaces than the main-chain segments.

In this paper we have assumed that the solution of equilibrium polymers is always in full equilibrium with a bulk solution (i.e., the chemical potential remains constant upon variation of d). This is justified if the timescale of variation of the separation between the two surfaces is much longer than the time needed for polymer to desorb and diffuse out of the gap. For strongly adsorbed polymer layers, however, desorption may be very slow, and full equilibrium may not be maintained (although for equilibrium polymers this may be easier than for ordinary polymers because the chains can break and recombine). In order to describe situations where equilibrium is not maintained, it is usually assumed that the amount of polymer in the gap stays fixed for all separations, while the segments are still allowed to redistribute between tails, loops, and trains (restricted equilibrium). This assumption leads to repulsive interactions between two surfaces covered with adsorbed polymer layers.¹ In the present model, it is straightforward to incorporate restricted equilibrium conditions. The parameter μ in Eq. (12) can then be considered as a Lagrange multiplier associated with the constant amount of polymer in the gap (rather than the chemical potential). It has been shown that for nonadsorbing equilibrium polymers restricted equilibrium results in repulsive surface forces.¹⁸ So far, we have not considered restricted equilibrium conditions.

Furthermore, we have neglected the effect of ring formation, both in the bulk and in the gap. It is expected that rings behave differently in gaps than open chains, because the loss of conformational entropy is smaller for a confined ring than for a confined open chain of the same length.²³ The approach followed in this paper could, however, easily be extended to take into account the formation of rings.

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