Polymer Bridging between Two Parallel Plates

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ABSTRACT: In this paper we study bridges formed by polymers between two parallel plates. We define two fundamental lengths, $\bar{N}$ and $\tilde{N}$, corresponding respectively to the length and the density of bridges. We develop methods to calculate these lengths for a single ideal long chain and for chains in a semidilute polymer solution. We note the formal mathematical analogy with the quantum tunneling problem and the opportunity to borrow techniques and results from there. We obtain analytic results in various limits, and we propose a blob picture to understand these results.

I. Introduction

When two solid surfaces immersed in a polymer solution are close enough to one another, some of the polymer chains will have contacts on both surfaces, forming "bridges" between them. On a time scale sufficiently short that the surface contacts do not break and re-form, these bridges will exhibit the rubber elasticity associated with a polymer chain whose ends are anchored, giving rise to an attractive force between the surfaces. Indeed, in the numerical study of Scheutjens and Fleer[1] the onset of attraction between two surfaces is always identified with the appearance of bridges. If we put a sufficiently high density of colloidal particles into a polymer solution, the bridges formed by polymers between these particles may eventually percolate into an elastic network and the system will go through a gelation transition. In a colloidal solution stabilized by polymers bridging will be an important physical process in the control of gelation and flocculation of the system.

The influence of bridging has also been frequently invoked to explain phenomena observed in measurements of force between the surfaces.[2–4] For example, when two such surfaces in a polymer solution are brought closer together, the force between them is observed to increase monotonically, but if they are then pulled apart rapidly, the curve of force versus separation will not be retraced; the repulsion at each separation will always be weaker than it was in equilibrium. This hysteresis phenomenon has been attributed to bridging. If the surfaces are decompressed so rapidly that the bridges are unable to relax to their equilibrium configurations at all separations, the chain elasticity of the excess bridges will effectively reduce the repulsive force. One other phenomenon that might be due to bridging is the observed attraction between two partially incubated surfaces;[5] at equilibrium only *repulsive* forces are found.[3]

There are two important aspects essential to the understanding of the effects of bridging on forces between surfaces. For the static behavior we require a knowledge of the average length and density of the bridges, while for the dynamical features we need to know the time scales for the establishment and relaxation of a bridge. In this paper, we shall focus on the static part of the problem.

In ref 6 numerical results have been obtained for the bridging size of one infinitely long ideal chain between two parallel plates. Our model here gives simple and *analytic* results. It is also more general than the approach of ref 6, since we examine not only the length but also the density of bridges, and we extend the treatment from single to semidilute solutions of interacting chains.

In section II, we first introduce the two fundamental lengths in bridging problems: $\bar{N}$ gives the average length of the bridges, while $\tilde{N}$, the average length between bridges, determines the density of bridges per unit surface area. We then propose a scheme to calculate $\tilde{N}$ and $\bar{N}$ by considering a single chain between two parallel surfaces subject to a general potential. The propagator approach of Edwards is used. An interesting feature of this scheme is that, since the propagator equation has the structure of a Schrödinger equation, there is a close formal analogy between the problems of polymer bridging and quantum tunneling. In section III, we apply this scheme to the infinitely long single ideal chain. The limits of weak and strong adsorption are treated analytically. Section IV is an extention to semidilute polymer solutions. There we use the standard mean field approximation to treat the excluded volume interactions. We study various regimes corresponding to different relative sizes of the separation between the plates, the correlation length of the polymer solution, and the length scale characterizing the attraction of the plates. In section V, we summarize the results for various physical situations and propose a blob picture to understand these results in a more intuitive way.

II. Formulation

We consider a single polymer chain between two parallel plates in a polymer solution. The potential acting on that chain is assumed to be $V(z)$, where z is the coordinate perpendicular to the plates. If we look at the configurations of the chain, we will find that certain chain sections link the two surfaces, making "bridges" between them (see Figure 1). A bridge is defined as a path between the surfaces which contacts them only at the two end points, such as the segment BC in Figure 1. The number of monomers forming a bridge is called the length of that bridge; its average value for the system is denoted by $\bar{N}$. The elasticity of a bridge is essentially determined by this length. There is another fundamental length for these problems, that *between* bridges, which we will denote $\tilde{N}$. If we look between any two consecutive bridges,

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we will see sequences of trains and loops of chains on one surface. $\tilde{N}$ is then the length that includes a bridge plus the trains and loops between this bridge and the previous one. A chain with molecular weight N and average length between bridges $\tilde{N}$ forms $N/\tilde{N}$ bridges between the two surfaces. $\tilde{N}^{-1}$ is then the bridging probability per monomer. We want to emphasize the distinction between $\bar{N}$ and $\tilde{N}$ here. In Figure 1 the bridge length, $\bar{N}$, corresponds to the segment from point B to C, whereas $\tilde{N}$ corresponds to the segment from A to C. At equilibrium, the statistical averages of $\bar{N}$ and $\tilde{N}$ depend on the potential $V(z)$ and the separation $2h$ of the two plates.

Let us consider first the calculation of $\tilde{N}$. If we adopt the lattice model of polymers, chain configurations can be described as walks on a lattice with lattice parameter equal to the monomer size a and with coordination number (i.e., number of nearest neighbors to each lattice point) ζ. The statistical weight associated with all configurations linking two planes z and z' in N steps is proportional to

$$G_N(z,z') = \zeta^{-N}\sum \exp\{-\beta[V(z) + V(z_2) + V(z_3) + \ldots + V(z_{N-1}) + V(z')]\} \quad \text{(II.1)}$$

where the sum is taken over all possible walks linking two planes at z and z'. Among the complete set of such walks, there are some that pass through z' for the first time at their final step. The statistical weight associated with these first passage paths from plane z to plane z' in N steps is

$$f_N(z,z') = \zeta^{-N}\sum{}' \exp\{-\beta[V(z) + V(z_2) + V(z_3) + \ldots + V(z_{N-1}) + V(z')]\} \quad \text{(II.2)}$$

where the prime indicates that the sum is taken over paths which do not reach z' before the final step. There is a simple relation between G_N and f_N:

$$G_N(z,z') = \sum_{N'=0}^{N} f_{N'}(z,z')G_{N-N'}(z',z') \quad \text{(II.3)}$$

(where $G_0(z,z) \equiv 1$).

The length between bridges $\tilde{N}$ is associated with these first passage configurations, in which walks starting from one surface are allowed to come back to the surface any number of times before reaching the other one for the first time at the final step. The probability of making a first passage from plane z to z' in the first N' steps of a total walk of N^* steps is proportional to

$$P_{N'}(z,z') = \frac{f_{N'}(z,z')\int \mathrm{d}z_0\, G_{N^*-N'}(z',z_0)}{\int \mathrm{d}z_0\, G_{N^*}(z,z_0)} \quad \text{(II.4)}$$

where the integral on z_0 is over the full allowed range of z in the problem. The sum

$$P(z,z') = \sum_{N'=0}^{N^*} P_{N'}(z,z') \quad \text{(II.5)}$$

gives the total probability of bridging between z and z' within N^* steps (with a path that begins at z). In the limit $N^* \to \infty$, an infinitely long chain, this total probability approaches unity for this problem of two parallel plates at finite separation. Thus $P_{N'}$ in eq II.4 is the normalized probability in this case. The statistical average of N' then gives the average length between bridges $\tilde{N}$:

$$\tilde{N} = \sum_{N'=0}^{\infty} N'P_{N'}(z,z') \quad \text{(II.6)}$$

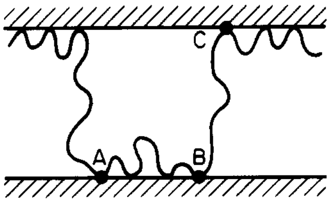

Figure 1. Typical bridging configuration. The bridge itself, of length defined to be $\bar{N}$, is the segment BC; the segment AC, of length $\tilde{N}$, is the section of the polymer between successive bridges.

In principle, once G_N is known, we can find $\tilde{N}$ from eq II.3–II.6. For the usual situation, when all physical quantities vary slowly on the spatial scale of the monomer length a, it can be demonstrated that $G_N(z,z')$, the statistical weight for a polymer to proceed from a point z to z' in N steps is given by the solution of a Schrödinger-like equation[7]

$$-\frac{\partial G}{\partial N} = -\frac{a^2}{6}\nabla^2 G + \frac{V}{T}G \equiv \mathcal{H}G \quad \text{(II.7)}$$

where V is an external potential acting on each monomer. The boundary condition in N is that $G_N(\vec{r},\vec{r}\,') \to \delta(\vec{r} - \vec{r}\,')$ in the limit $N \to 0$; the spatial boundary conditions at z_a and z_b are set by the interactions of the polymer with the surfaces there. The cylindrical symmetry of this problem makes the planar (xy) and z dependences in $G_N(\vec{r},\vec{r}\,')$ separable; the z-dependent factor may be expressed as

$$G_N(z,z') = a\sum_m \phi_m^*(z')\phi_m(z)e^{-N\omega_m} \quad \text{(II.8)}$$

where the φ_m are the normalized (xy independent) eigenfunctions of the Hermitian operator $\mathcal{H}$, with eigenvalues ω_m:

$$\omega_m\phi_m = \mathcal{H}\phi_m; \quad \int \mathrm{d}z\, |\phi_m(z)|^2 = 1 \quad \text{(II.9)}$$

When $N \to \infty$, because of the exponential dependence on N in eq II.8, G_N is dominated by the first term in the sum, which corresponds to the ground state of $\mathcal{H}$. Using this result, from eq II.4 we can write the bridging probability function $P_{N'}$ in the limit of an infinitely long chain in the simple form

$$P_{N'}(z,z') \simeq f_{N'}(z,z')e^{N'\omega_0} \quad \text{(II.10)}$$

where ω_0 is the ground-state energy of $\mathcal{H}$. We have assumed the symmetry of the two planes z and z' (the physically identical planes of the problem of interest impose identical spatial boundary conditions), so that $\phi_0(z)/\phi_0(z') = 1$.

Now we define two generating functions from $f_N(z,z')$ and $G_N(z,z')$:

$$F_\alpha(z,z') = \sum_{N=0}^{\infty} f_N(z,z')\alpha^N; \quad Q_\alpha(z,z') = \sum_{N=0}^{\infty} G_N(z,z')\alpha^N \quad \text{(II.11)}$$

The convolution relation between f_N and G_N in eq II.3 then turns into a simple algebraic relation between their generating functions:

$$F_\alpha(z,z') = \frac{Q_\alpha(z,z')}{Q_\alpha(z',z')} \quad \text{(II.12)}$$

Once F_α is found from G_N using this equation, the length between bridges $\tilde{N}$ will be given as

$$\tilde{N} = \sum_{N'=0}^{\infty} N' f_{N'}(z,z') e^{N'\omega_0} = \alpha \left. \frac{\mathrm{d}F_\alpha(z,z')}{\mathrm{d}\alpha} \right|_{\alpha=\exp(\omega_0)} \qquad \text{(II.13)}$$

We choose the origin of z midway between the plates, which are then located at $z = \pm h$. Then we can invoke the standard result that the states $\phi_{2m}(z)$ have even and the states $\phi_{2m+1}(z)$ odd parity (m = 0, 1, 2, 3, ...) in z. Using eq II.11, II.12, and II.8, we then obtain

$$F_\alpha(-h,h) = \frac{\sum_{m=0}^{\infty} (-1)^m \phi_m^{\,2}(h)/(1 - \alpha e^{-\omega_m})}{\sum_{m=0}^{\infty} \phi_m^{\,2}(h)/(1 - \alpha e^{-\omega_m})} \qquad \text{(II.14)}$$

Here we have explicitly carried out the sums over N in eq II.11, which are simple geometric series. As is clear from eq II.13, we are particularly interested in the generating function F_α and its derivative at the point $\alpha = e^{\omega_0}$. The $m = 0$ term in the numerator and denominator of eq II.14 each diverges at that point, though the ratio is, of course, well-behaved. We therefore multiply each by the factor $1 - \alpha e^{-\omega_0}$ to remove the divergence. We can then expand to first order in the small quantities $(1 - \alpha e^{-\omega_0})/(1 - \alpha e^{-\omega_m})$ (for $m \neq 0$):

$$F_\alpha(-h,h) \simeq 1 - 2\sum_{m=1}^{\infty} \left[\frac{\phi_{2m-1}(h)}{\phi_0(h)} \right]^2 \frac{1 - \alpha e^{-\omega_0}}{1 - \alpha e^{-\omega_{2m-1}}} \qquad \text{(II.15)}$$

Insertion of this expression into eq II.13 gives the length between bridges

$$\tilde{N} = \sum_{m=1}^{\infty} \frac{2}{\exp(\Delta\omega_{2m-1}) - 1} \left[\frac{\phi_{2m-1}(h)}{\phi_0(h)} \right]^2 \simeq \sum_{m=1}^{\infty} \frac{2}{\Delta\omega_{2m-1}} \left[\frac{\phi_{2m-1}(h)}{\phi_0(h)} \right]^2 \qquad \text{(II.16)}$$

where $\Delta\omega_m \equiv \omega_m - \omega_0$, and in the final approximation we have used the fact that ordinarily $\Delta\omega \ll 1$ for the many small values of m which give the dominant contributions to the sum.

In most physical situations, the first term in the sum over m in eq II.16 dominates the contributions to $\tilde{N}$, so it is usually sufficient to write

$$\tilde{N} \simeq \frac{2}{\omega_1 - \omega_0} \left[\frac{\phi_1(h)}{\phi_0(h)} \right]^2 \qquad \text{(II.17)}$$

The length between bridges is inversely proportional to the energy splitting $\Delta\omega$ of the ground and first excited states in the approximation where only these two lowest energy states are retained, a familiar result[8] from the analogous quantum tunneling problem.

Now consider the length of the bridge $\bar{N}$, which is the average number of monomers per bridge. Suppose we have one chain with molecular weight N^*, which bridges (in general, multiply) between two plates at z_a and z_b. Consider a single bridge with N' monomers and assume that the two tails extending from the ends of that bridge at z_a and z_b consist of N_a and N_b monomers, respectively. The statistical weight associated with this configuration is proportional to

$$S(z_a,z_b) \propto \int \mathrm{d}z\, G_{N_a}(z,z_a) B_{N'}(z_a,z_b) \int \mathrm{d}z\, G_{N_b}(z_b,z) \qquad \text{(II.18)}$$

where $N_a + N' + N_b = N^*$, and the integral on z is over the whole accessible range of z in the problem: $z_a \leq z \leq z_b$. Here G_N is the usual statistical weight function (II.1) for polymers between the two plates; in eq II.18 there is one such factor for each of the two tails of the chain. The remaining factor, $B_{N'}(z_a,z_b)$, is the statistical weight associated with the bridging configurations

$$B_{N'}(z_a,z_b) = \zeta^{-N'} {\sum}' \exp\{-\beta[V(z_a) + V(z_1) + V(z_2) + \ldots + V(z_{N'-2}) + V(z_b)]\} \qquad \text{(II.19)}$$

where the prime indicates that the sum is taken over configurations that contact the surfaces only at the two end points—i.e., $z_a + a \leq z_1, z_2, \ldots, z_{N'} \leq z_b - a$ in the summation (where a is the monomer size). Therefore apart from the two end points, monomers on the bridge are bounded by two virtual surfaces, one at a single monomer layer above the bottom plate and the other at one monomer layer below the upper plate. These virtual surfaces serve as geometric barriers and thus have no explicit interaction with the monomers. If the statistical weight function for polymers between the two virtual surfaces is $\bar{G}_N(z,z')$, we will have

$$B_{N'}(z_a,z_b) = \zeta^{-N'} \exp\{-\beta[V(z_a) + V(z_b)]\} \bar{G}_{N'-2}(z_a + a, z_b - a) \simeq \bar{G}_{N'}(z_a,z_b) \qquad \text{(II.20)}$$

where the final approximation relies on the facts that the separation between two plates $z_b - z_a \gg a$ and that usually $\beta V(z) \ll 1$ and $N' \gg 1$, so that we may neglect end-point effects. The function $\tilde{G}_N$ is given by the general differential equation (II.7), but with the spatial boundary conditions at z_a and z_b now those appropriate to the virtual noninteractive, rather than to the physical, surfaces: $\partial\bar{G}_N/\partial z = 0$.

The explicit solution for the statistical weight function G_N is written in eq II.8 in terms of the eigenfunctions of $\mathcal{H}$ (with appropriate boundary conditions). In the limit of a long chain, we assume that the tails are long enough that we need only retain the dominant ground-state terms in both G_{N_a} and G_{N_b} in eq II.18. The contributions from configurations where the bridge is at one end of the long chain are relatively small and may be neglected. Hence the probability of having N' monomers on the bridge is proportional to

$$S_{N'} \propto \bar{G}_{N'}(z_a,z_b) e^{N'\omega_0} \qquad \text{(II.21)}$$

where ω_0 is the ground-state energy for $\mathcal{H}$ with boundary conditions appropriate to the two physical plates. As we will see in detail later, the statistical weight factor $\bar{G}_{N'}(z_a,z_b)$ favors additional monomers on the bridge for the sake of higher entropy. The exponential term, on the other hand, promotes additional monomers in the tails to take advantage of the attraction to the plates. The average length of bridges $\bar{N}$ is given by the balance of these competing entropic and energetic effects so as to minimize the free energy. It may be calculated from the equation

$$\bar{N} = \sum_{N'=0}^{\infty} N' S_{N'} \Big/ \sum_{N'=0}^{\infty} S_{N'} \qquad \text{(II.22)}$$

The results (II.17) and (II.22) are the key equations in this paper. In sections III and IV, respectively, we will consider bridging for single chains and in semidilute solutions, using the formalism discussed here.

III. Single Chain Bridging

In this section, we will consider bridging between two parallel plates by one ideal long chain. We neglect the excluded volume interactions between monomers and assume that the attraction of the plates is sufficiently weak that the adsorption layer thickness is much larger than the monomer size a. We assume further that the attraction is short ranged (one monomer length), so that we can replace the attraction of the plate by a boundary condition first proposed by de Gennes.[9]

Consider first the length between bridges $\tilde{N}$. The eigenequations that give ϕ and ω are

$$-\frac{\alpha^2}{6}\frac{d^2\phi}{dz^2} = \omega\phi \qquad \text{(III.1)}$$

subject to the boundary conditions

$$\left.\frac{1}{\phi}\frac{d\phi}{dz}\right|_{z=\pm h} = \pm\kappa \qquad \text{(III.2)}$$

where κ is the parameter that describes the interaction between the wall and monomers; it is positive when attraction dominates. In the single surface adsorption problem, $D \equiv \kappa^{-1}$ gives the thickness of the adsorption polymer layer. The weak adsorption condition is thus $\kappa a \ll 1$.

The form of eq III.1 and the symmetry of the boundary condition eq III.2 give for the eigenfunctions ϕ and eigenvalues ω the solutions

$$\phi_\pm(z) = A_\pm(e^{\alpha_\pm z} \pm e^{-\alpha_\pm z}); \quad \omega_\pm = a^2\alpha_\pm{}^2/6 \qquad \text{(III.3)}$$

where A_+ and A_- are normalization factors. The eigenvalues $\alpha_\pm$ are determined by the boundary conditions

$$\coth(\alpha_+ h) = (\alpha_+ h)/\kappa h \qquad \text{(III.4)}$$

$$\tanh(\alpha_- h) = (\alpha_- h)/\kappa h \qquad \text{(III.5)}$$

In general, these transcendental equations can be solved numerically. However, it is also instructive to consider analytically the two limits of noninteractive walls ($\kappa = 0$) and strong attraction ($\kappa h \gg 1$).

If the plates neither attract nor repel the chain ($\kappa = 0$), we can find the full set of eigenfunctions and eigenvalues directly from eq III.1 and III.2

$$\phi_0(z) = 1/\sqrt{2h}; \quad \omega_0 = 0$$

$$\phi_{2m-1}(z) = \sqrt{\frac{1}{h}}\sin\frac{(2m-1)\pi z}{2h}; \quad \omega_{2m-1} = \frac{(2m-1)^2\pi^2a^2}{24h^2}$$

$$\phi_{2m}(z) = \sqrt{\frac{1}{h}}\cos\frac{m\pi z}{h}; \quad \omega_{2m} = \frac{m^2\pi^2a^2}{6h^2} \qquad \text{(III.6)}$$

where $m = 1, 2, 3, ...$ From eq II.16 we find

$$\tilde{N} \approx \frac{96h^2}{\pi^2a^2}\sum_{m=1}^{\infty}\frac{1}{(2m-1)^2} = 12(h/a)^2 \qquad \text{(III.7)}$$

If we keep only the first term in the sum (the usual two level approximation), the result for $\tilde{N}$ will be

$$\tilde{N} \simeq \frac{2}{\omega_1 - \omega_0}\left[\frac{\phi_1(h)}{\phi_0(h)}\right]^2 = 9.7(h/a)^2 \qquad \text{(III.8)}$$

The error from neglecting all but the first two levels is less than 20%. Moreover, when we turn on the attraction to the wall, the ground and first excited states will become bound ($\alpha_\pm$ real), whereas all higher states will be unbound ($\alpha_\pm$ pure imaginary). The energy separation between the first two levels and the rest will increase with the attraction of the wall, so that the two level approximation will become increasingly accurate. In the strongly attractive wall limit, it can be taken as essentially exact.

To calculate $\bar{N}$ is particularly simple in the limit of noninteractive plates. The bridging configurations are nothing but first passage configurations from a virtual surface one monomer layer above the bottom plate to the upper plate, apart from one monomer that connects the bottom plate with the virtual surface. Since the virtual surface is also noninteractive with the chain, we have the same problem as for the calculation of $\tilde{N}$ except that the distance between surfaces is reduced by one monomer length. The separation between the two boundaries is now $2h - a$ instead of $2h$. $\bar{N}$ can then be obtained directly by making this substitution in eq III.7:

$$\bar{N} = 3\left(\frac{2h-a}{a}\right)^2 \approx 12\left(\frac{h}{a}\right)^2 - 12\frac{h}{a} \qquad \text{(III.9)}$$

The values of $\bar{N}$ and $\tilde{N}$ are very close in this limit; their difference is linear in h/a. The physical implications of this result will be discussed later.

Consider now the limit of strong attraction. Since $\kappa h \gg 1$ and eq III.4 and III.5 then give $\alpha_\pm h \sim \kappa h$ for the lowest (real) eigenvalues, we may expand the hyperbolic functions in these equations to lowest order in $\exp(-\alpha_\pm h)$. We find that the first two states are

$$\phi_\pm(z) = \sqrt{\bar{\kappa}}e^{-\kappa h}(e^{\kappa z} \pm e^{-\kappa z}); \quad \omega_\pm \approx -\kappa^2a^2(1 \pm 4e^{-2\kappa h})/6 \qquad \text{(III.10)}$$

We note that the separation between first and second excited states, the latter with $\omega \gtrsim 0$, is of order $(\kappa a)^2$, so that the two level approximation improves with increasing attraction, as foreseen above. These two lowest states yield

$$\Delta\omega = \omega_- - \omega_+ = (4\kappa^2a^2/3)e^{-2\kappa h}; \quad [\phi_-(h)/\phi_+(h)]^2 \approx 1 \qquad \text{(III.11)}$$

so from eq II.17 the average length between bridges $\tilde{N}$ in this limit of strong attraction ($\kappa h \gg 1$) will be given by

$$\tilde{N} \approx \frac{2}{\Delta\omega}\left[\frac{\phi_-(h)}{\phi_+(h)}\right]^2 = \frac{3}{2(\kappa a)^2}e^{2\kappa h} = \frac{3}{2}\left(\frac{D}{a}\right)^2 e^{2h/D} \qquad \text{(III.12)}$$

We find an exponential form familiar from the analogous quantum tunneling problem.

We now calculate the bridge length $\bar{N}$ in the strong attraction limit. As we pointed out in section II, the statistical weight function $\bar{G}_N$ satisfies the Schrödinger-like equation (II.7), whose general solution can be written as

$$\bar{G}_N(z,z') = a\sum_m \bar{\phi}_m(z)\bar{\phi}_m{}^*(z')e^{-N\bar{\omega}_m} \qquad \text{(III.13)}$$

where $\bar{\phi}_m(z)$ and $\bar{\omega}_m$ are given by

$$-\frac{a^2}{6}\frac{d^2\bar{\phi}}{dz^2} = \bar{\omega}\bar{\phi} \qquad \text{(III.14)}$$

subject to the boundary conditions

$$\left.\frac{1}{\bar{\phi}}\frac{d\bar{\phi}}{dz}\right|_{z=0,2h} = 0 \qquad \text{(III.15)}$$

For calculational convenience we have shifted the origin of coordinates to the position of the lower plate. From the last two equations we find

$$\bar{\phi}_0(z) = 1/\sqrt{2h}; \quad \bar{\omega}_0 = 0$$

$$\bar{\phi}_m(z) = \sqrt{\frac{1}{h}} \cos \frac{m\pi z}{2h}; \quad \bar{\omega}_m = \frac{m^2\pi^2a^2}{24h^2} \qquad \text{(III.16)}$$

where $m = 1, 2, 3, ...$ Hence from eq III.13 we obtain for $\bar{G}_N$

$$\bar{G}_N(0,2h) = \frac{a}{2h}[1 + 2\sum_{m=1}^{\infty}(-1)^m \exp\{-Nm^2\pi^2a^2/24h^2\}] \qquad \text{(III.17)}$$

$$\bar{G}_N(0,2h) = \frac{a}{4hi} \oint \mathrm{d}m \, \frac{e^{-\alpha m^2}}{\sin m\pi} \qquad \text{(III.18)}$$

where the contour encloses the whole real axis and $\alpha \equiv N\pi^2a^2/24h^2$. Since there are no poles in the finite part of the complex m-plane off the real axis, we can deform the contour to the two straight lines $\pm iA + m$ (with $-\infty < m < \infty$). The answer is, of course, independent of A, so we calculate in the limit of large A

$$\bar{G}_N(0,2h) \approx \frac{a}{h} \int_{-\infty}^{\infty} \mathrm{d}x \, e^{-\pi(A-ix)}e^{-\alpha(iA+x)^2} = \sqrt{\frac{24}{\pi N}} \exp\left[-\frac{6}{N}\left(\frac{h}{a}\right)^2\right] \qquad \text{(III.19)}$$

We see that indeed $\bar{G}_N$ is a Gaussian function of the plate separation h, as anticipated.[10]

The ground-state energy in the strong attraction limit is $\omega_0 = -(\kappa a)^2/6$, as we recall from eq III.10. Insertion of the expressions of $\bar{G}_N(0,2h)$ and ω_0 into eq II.21 yields the probability function of having N monomers on the bridge:

$$S_N = \left(\frac{24}{\pi N}\right)^{1/2} \exp\left\{-\frac{6h^2}{Na^2} - \frac{Na^2}{6D^2}\right\} \qquad \text{(III.20)}$$

Here $D = \kappa^{-1}$. Using eq II.22 and III.20, we find that the average length of bridges in this limit is

$$\bar{N} = \frac{6hD}{a^2} + \frac{3D^2}{a^2} \simeq 6hD/a^2 \qquad \text{(III.21)}$$

where we have used $h/D \gg 1$ in the final approximation. These formal results are readily interpreted in more intuitive physical terms. The two terms in the exponent of eq III.20 for the statistical weight are essentially contributions to the free energy of the polymer chain of N^* monomers confined between two planes at $z = \pm h$ and constrained to have a bridge N monomers in length. The first, of order h^2/Na^2, is the entropic contribution from the bridge (whose monomers are subject to no potential), and the second, of order $-(N^* - N)a^2/D^2$ (up to an additive constant), represents the average free energy of the rest of the $N^* - N$ monomers (negative, since it is arises from the attractive energy term). The optimum value of the bridge size N is then given by the minimization of this free energy:

$$\bar{N} \sim hD/a^2 \qquad \text{(III.22)}$$

The expression for $\bar{N}$ can also be written as

$$\bar{N} = 6\left(\frac{h}{a}\right)^2\left(\frac{D}{h}\right) \qquad \text{(III.23)}$$

Comparing this with eq III.9, we find that relative to the case of noninteractive plates, the average length of the bridges will be reduced by a factor of $2D/h$ in the presence of strong wall–monomer attractions. The further physical interpretation of this result and the others in this section will be explored in the Discussion (section V) along with corresponding results for the semidilute polymer solution, to which we turn our attention next.

IV. Bridging in Semidilute Solutions

In practice the isolated chain model of the previous section is usually an inadequate one. Therefore, we extend our calculation to bridging between two parallel plates in a semidilute polymer solution. If we concentrate on one specific chain, the new feature is that in addition to the attraction of the walls, the polymer chain also experiences repulsive interactions from the other chains. Using a standard mean field approximation, we assume that this interaction potential (in units of the temperature T) can be represented by $V = v\Phi$, where Φ is the local equilibrium concentration of monomers and v is the excluded volume parameter. The combination of this repulsive potential and the attractive wells near the surfaces form a more complicated potential barrier through which the chain tunnels to form the bridge.

The strength of the excluded volume repulsion is characterized by a correlation length[11] $\xi \equiv a/(3v\Phi_b)^{1/2}$, where Φ_b is the bulk concentration of the polymer solution. We then have three fundamental length scales in the problem: the separation between the surfaces $2h$, the bulk correlation length ξ, and a length $D \equiv \kappa^{-1}$ which characterizes the strength of the surface attraction. It is convenient and instructive in exploring the bridging behavior to consider separately the various possible regimes of relative size of these lengths.

(1) **$h < D, \xi$.** We first consider the case when h is the smallest length in the problem. The characteristic distance over which the energetics allow appreciable changes in concentration is larger than the length (h) available, so neither interaction with the walls nor the excluded volume repulsion can appreciably affect the polymer configuration. This implies that the characteristic bridging lengths are just those of the single ideal chain confined by noninteractive walls. From the previous section we have in this case the simple result

$$\bar{N} \simeq \tilde{N} \simeq 12(h/a)^2 \qquad \text{(IV.1)}$$

(2) **$h > \xi > D$.** We next consider the limit when the separation between the two plates is large, and the wall–monomer attraction is stronger than the excluded volume interaction. This limit is of particular practical interest; colloidal solutions stabilized by polymers, e.g., usually fall into this regime. Since the wall–monomer attraction is strong, there will be an accumulation of polymers near the surfaces, with a consequent increase in the mean field repulsion $V(z) = v\Phi(z)$ (relative to those in the middle region). The bridging configurations are, of course, significantly affected.

Within mean field theory, the concentration profile for a semidilute polymer solution in the vicinity of a wall is given by[11]

$$\Phi(z) = \Phi_b \coth^2\left(\frac{z + z_0}{\xi}\right) \qquad \text{(IV.2)}$$

where z is the distance from the wall and z_0 is determined by the boundary condition

$$-\frac{1}{\Phi}\frac{\mathrm{d}\Phi}{\mathrm{d}z}\bigg|_{z=0} = \kappa \qquad \text{(IV.3)}$$

In this limit, when $\kappa\xi \gg 1$, we find $z_0 \simeq \kappa^{-1} = \mathrm{D}$. From eq IV.2, the length scale over which the concentration falls off from the wall is found always to be the correlation length ξ. Hence when $h \gg \xi$, the concentration profile between two walls may be approximated by the superposition of hyperbolic functions of the form (IV.2) falling off from each wall to approach the same asymptotic value at the midplane. The mean field potential $V(z)$ can then be expressed as the sum of contributions from quasi-independent surfaces

$$V(z) \simeq V_0(h+z) + V_0(h-z) \qquad \text{(IV.4)}$$

where $V_0(z)$ has the form

$$V_0(z) = v\Phi_b \coth^2\left(\frac{z+z_0}{\xi}\right) = {}^1/_3\left(\frac{a}{\xi}\right)^2 \coth^2\left(\frac{z+z_0}{\xi}\right) \qquad \text{(IV.5)}$$

Apart from the regions within a distance ξ from the two walls, the mean field excluded volume potential is found to be essentially constant over the volume, with a value $v\Phi_b = ({}^1/_3)(a/\xi)^2$.

In order to calculate $\tilde{N}$ we need the eigenstates for the Schrödinger equation (II.7) with the mean field potential $V(z)$ given by eq IV.4 and with boundary conditions for two attractive surfaces as given by eq III.2. This one-dimensional Schrödinger equation for two symmetric potential wells with an intervening potential barrier has been studied extensively in quantum mechanics[8] to describe the process of quantum tunneling. We will reformulate the method used there to find the lowest two eigenstates.

The ground state in a single potential well is ψ, with eigenvalue ω'; we normalize ψ within this well ($0 \le z \le h$). When the barrier is sufficiently large that the bridging probability (analogous to the quantum tunneling probability) is much smaller than 1, the two lowest eigenstates may be approximated by the symmetric and antisymmetric combinations of $\psi(z)$ and $\psi(-z)$:

$$\phi_0(z) \simeq \frac{1}{\sqrt{2}}[\psi(z) + \psi(-z)]; \quad \phi_1(z) \simeq \frac{1}{\sqrt{2}}[\psi(z) - \psi(-z)] \qquad \text{(IV.6)}$$

These states ϕ_0 and ϕ_1 are each normalized over the full region $-h \le z \le h$ (within the approximation that the product $\psi(z)\psi(-z)$, small everywhere, can be neglected).

The eigenequations for ϕ_0 and ϕ_1 are

$$\phi_0'' + \frac{6}{a^2}[\omega_0 - V(z)]\phi_0 = 0 \qquad \text{(IV.7)}$$

$$\phi_1'' + \frac{6}{a^2}[\omega_1 - V(z)]\phi_1 = 0 \qquad \text{(IV.8)}$$

If we multiply eq IV.8 by ϕ_0 and eq IV.7 by ϕ_1, subtract them, and then integrate from 0 to h, we find

$$\Delta\omega_1 \equiv \omega_1 - \omega_0 = -\frac{2a^2}{3}\psi(0)\psi'(0) \qquad \text{(IV.9)}$$

Here we have used the properties, from the definition (IV.6), that $\phi_0 \simeq (2)^{1/2}\psi$ and $\phi_0' = 0$ at $z = 0$. We have also made use of the symmetry of boundary conditions for ψ at the two surfaces.

The single potential well ground state ψ is determined by its eigenequation

$$\psi' + \frac{6}{a^2}\left[\omega' - \frac{1}{3}\left(\frac{a}{\xi}\right)^2 \operatorname{csch}^2\left(\frac{z+z_0}{\xi}\right)\right]\psi = 0 \qquad \text{(IV.10)}$$

(we have now chosen the zero of energy so that the constant potential far from the walls is zero: $V \sim \coth^2 x - 1 = \operatorname{csch}^2 x$), with boundary condition

$$\left.\frac{1}{\psi}\frac{\mathrm{d}\psi}{\mathrm{d}z}\right|_{z=h} = \kappa \qquad \text{(IV.11)}$$

where the potential in eq IV.10 is given by eq IV.5. Equation IV.10 may be turned into a hypergeometric equation after changing variables,[8] and in the limit of strong attraction ($\kappa\xi \gg 1$), neglecting terms of order $(\kappa\xi)^{-2}$, we find

$$\psi(z) \simeq \left[\xi\sqrt{\kappa}\sinh\left(\frac{h+\kappa^{-1}-z}{\xi}\right)\right]^{-1}; \quad \omega' \simeq -\frac{1}{6}\left(\frac{a}{\xi}\right)^2 \qquad \text{(IV.12)}$$

Inserting this expression for ψ into eq IV.9, we find that the separation between the lowest two levels is

$$\Delta\omega \simeq \frac{2a^2}{3\kappa\xi^3}e^{-2h/\xi} \qquad \text{(IV.13)}$$

From eq IV.6, we further have

$$\frac{\phi_1(h)}{\phi_0(h)} = \frac{\psi(h) - \psi(-h)}{\psi(h) + \psi(-h)} \simeq 1 \qquad \text{(IV.14)}$$

Within the two level approximation, $\tilde{N}$ may then be obtained by using eq IV.13 and IV.14 in eq II.17. Hence, for a semidilute polymer solution between two parallel plates, in the limit when the surface–monomer attraction is stronger than the excluded volume repulsion, our mean field calculations predict that the average length between bridges is given by

$$\tilde{N} = \frac{3\kappa\xi^3}{2a^2}e^{2h/\xi} = \frac{3}{2}\kappa\xi\left(\frac{\xi}{a}\right)^2 e^{2h/\xi} \qquad \text{(IV.15)}$$

We can further estimate the size of the correction to the two-level approximation. The solutions ϕ_0 and ϕ_1 are bound states ($\omega' < 0$), arising from the splitting of the single well ground state ψ in the presence of bridging. The next excited state is found to be unbound; the eigenstate extends importantly over the whole region between the plates, so the energy can be estimated well away from the surfaces, where it is essentially all "kinetic" and therefore, as usual, of order $(a/h)^2 \ll (a/\xi)^2$). Thus, its separation from the ground state is $\omega_2 - \omega_0 \gtrsim (a/\xi)^2/6$, which is greater than the separation of the lowest two levels, (IV.13), by the very large factor $\kappa\xi \exp(2h/\xi)$. Higher lying states are also, of course, unbound, so their eigenvalues ω_n for $n > 2$, are separated from the second excited state by amounts approximately those of the constant potential case: $\omega_n - \omega_2 \sim (na/h)^2$. Then, from eq II.16, the contribution from these higher excited states to $\tilde{N}$ is bounded from above by

$$\sum_{m=1}^{\infty} 2/(\omega_{2m-1} - \omega_0) \sim (h/a)^2$$

The ratio of this to the contribution from the lowest two levels (IV.15) is then less than $(1/\kappa\xi)(h/\xi)^2 e^{-2h/\xi} \ll 1$ and can indeed be neglected; the two-level approximation is excellent here.

We may compare the result (IV.15) with $\tilde{N}$ in eq III.12 for a single chain between two strongly attractive plates. We find that the length scale in the dominant exponential term, originally D in the single chain problem, is replaced by the bulk correlation length ξ due to the repulsion from other chains.

To find the average length of a bridge $\bar{N}$ in this limit, we need first to derive the function $\tilde{G}_N(0,2h)$ in eq II.21. Here this function is the statistical weight function for a chain between two noninteractive surfaces that replace the two plates, and the potential between the surfaces is kept unchanged as $V(z)$ (eq IV.4). Over most of the region between the surfaces, the potential is nearly constant, but within a distance ξ from each surfaces we have two repulsive barriers. We now argue that as long as the barriers are narrow compared to the separation of the surfaces ($\xi \ll 2h$), their effect on the N dependence of $\bar{G}_N(0,2h)$ is negligible up to order ξ/h. In the absence of potential barriers (the potential $V(z)$ is constant everywhere between the two surfaces), $\bar{G}_N(0,2h)$ is given directly by eq III.19. On the other hand, in the limit of high barriers (i.e., $V(z) \approx V_0 \gg 1$ for z within a correlation length ξ of either surface, again with the energy referred to zero at midplane: $V(0) = 0$), then the Boltzmann statistical weighting of configurations will assure the quickest possible—i.e., straight line—passage through the high potential region, and $\bar{G}_N(0,2h)$ can be written as

$$\bar{G}_N(0,2h) \simeq \left(\frac{6}{\pi N}\right)^{1/2} \exp\{-6(h-\xi)^2/Na^2\} e^{-N\upsilon\phi_b} e^{-2V\xi/a} \qquad \text{(IV.16)}$$

Except for the final N-independent factor, this function is equivalent to the barrier-free result (III.19) up to corrections of order ξ/h. To this order we find that the probability function of having N monomers on the bridge (see eq II.21) is

$$S_N \propto \left(\frac{6}{\pi N}\right)^{1/2} \exp\left\{-\frac{6h^2}{Na^2} - \frac{Na^2}{6\xi^2}\right\} \qquad \text{(IV.17)}$$

where we have used the result (IV.12) for the eigenvalue: $\omega' \approx -a^2/6\xi^2$. The average length of a bridge is then given by eq II.22

$$\bar{N} = \frac{6h\xi}{a^2} + \frac{3\xi^2}{a^2} \simeq \frac{6h\xi}{a^2} \qquad \text{(IV.18)}$$

where we have used the fact that $h/\xi \gg 1$ in the current limit to neglect the second term in the final approximation. Note the similarity in form between this expression and eq III.21. The physical implication behind this similarity will be further explored in the discussion.

(3) $h > D > \xi$. In this limit, the separation between two plates is still large, but the wall-monomer attraction is now weaker than the excluded volume interaction. The concentration profile of polymers will be only weakly perturbed from its bulk value by the attraction to the walls. Since the walls are well separated, we can simply superimpose the small density changes due to each of the walls alone. For polymers in contact with a single wall, since $\kappa\xi \ll 1$, the concentration profile can be derived by expanding the general solution of eq IV.2 to lowest order in $\kappa\xi$:

$$\Phi(z) \approx \Phi_b[1 + \kappa\xi e^{-2z/\xi}] \qquad \text{(IV.19)}$$

Here z represents the distance from the surface. The mean field potential associated with this profile is then

$$V_0(z) = \frac{1}{3}\left(\frac{a}{\xi}\right)^2 [1 + \kappa\xi e^{-2z/\xi}] \qquad \text{(IV.20)}$$

A small exponential term, of spatial range $\xi \ll h$, is added to the bulk constant term.

Since the separation between the two surfaces is still the largest length in the problem, the method we used above in the limit $h > \xi > D$ is still applicable. Consider first the length between bridges $\tilde{N}$. As we pointed out before, the lowest two levels for the two plates problem are approximately the symmetric and antisymmetric combinations of the ground state for a single surface. This ground state is determined by a Schrödinger equation with potential $V_0(z)$ now given by eq IV.20. If, for convenience, we again choose the energy zero so that the constant bulk term in $V_0(z)$ vanishes, the eigenequation for this ground state ψ becomes

$$\psi'' + \frac{6}{a^2}\left[\omega' - \frac{\kappa a^2}{3\xi} e^{-2z/\xi}\right]\psi = 0 \qquad \text{(IV.21)}$$

with a boundary condition

$$\left.\frac{1}{\psi}\frac{\mathrm{d}\psi}{\mathrm{d}z}\right|_{z=0} = -\kappa \qquad \text{(IV.22)}$$

Here we have chosen coordinates with the wall located at $z = 0$ and polymers in the region $z \geq 0$. After a change of variable, $\bar{z} \equiv (2\kappa\xi)^{1/2} \mathrm{e}^{-z/\xi}$, eq IV.21 may be reduced to a Bessel equation:

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}\bar{z}^2} + \frac{1}{\bar{z}}\frac{\mathrm{d}\psi}{\mathrm{d}\bar{z}} - \left(1 + \frac{\upsilon^2}{\bar{z}^2}\right)\psi = 0 \qquad \text{(IV.23)}$$

where the renormalized eigenvalue is $\upsilon^2 \equiv -6\omega'\xi^2/a^2$. The finite solution for $z \geq 0$ is a modified Bessel function:

$$\psi \sim I_\upsilon(\bar{z}) \qquad \text{(IV.24)}$$

The eigenvalue υ is determined from the boundary condition eq IV.22:

$$I_\upsilon'(\sqrt{2\kappa\xi})/I_\upsilon(\sqrt{2\kappa\xi}) = \sqrt{\kappa\xi/2} \qquad \text{(IV.25)}$$

Since $(2\kappa\xi)^{1/2} \ll 1$, we may approximate $I_\upsilon(x)$ in eq IV.25 by its asymptotic expansion as $x \to 0$ to find

$$\upsilon \simeq \kappa\xi/2 \qquad \text{(IV.26)}$$

From eq IV.24 and IV.26 we then have for the ground-state solution to the single wall problem

$$\psi(z) \simeq \sqrt{\kappa} I_\upsilon(\bar{z}); \quad \omega' \simeq -(\kappa a)^2/24 \qquad \text{(IV.27)}$$

From the two surface problem the splitting of the two lowest levels is then given by eq IV.9

$$\Delta\omega_1 = -\frac{2a^2}{3}\psi(0)\psi'(0) \simeq \frac{1}{3}(\kappa a)^2 e^{-\kappa h} \qquad \text{(IV.28)}$$

Equation IV.14 for $\phi_1(h)/\phi_0(h)$, the ratio of the amplitudes of the gound and first excited state eigenfunctions at the surface, remains valid in this limit. Then from eq II.17 we find the length between bridges in this limit of $h > D > \xi$ to be

$$\tilde{N} = \frac{6}{(\kappa a)^2} e^{\kappa h} \simeq 6\left(\frac{D}{a}\right)^2 e^{h/D} \qquad \text{(IV.29)}$$

Finally we consider the length of a bridge $\bar{N}$ in this regime. Using the same argument that led to eq IV.16, we conclude that we may use the single chain result (III.19) for $\bar{G}_N(0,2h)$ as an approximation valid to order ξ/h. With this result and the value of the ground-state eigenvalue $\omega_0 = -(1/24)(a/D)^2$ from eq IV.27, we find from eq II.21 for the probability S_N of having N monomers on a bridge:

$$S_\mathrm{N} \propto N^{-1/2} \exp\left\{-\frac{6h^2}{Na^2} - \frac{Na^2}{24D^2}\right\} \qquad \text{(IV.30)}$$

From this expression and eq II.22, we find that the average length of a bridge in the regime $h \gg D \gg \xi$ is

$$\bar{N} = \frac{12hD}{a^2} + \frac{24D^2}{a^2} \simeq \frac{12hD}{a^2} \qquad \text{(IV.31)}$$

The results for $\tilde{N}$ and $\bar{N}$ here have the same functional dependences as those found above for a single chain between two strongly attractive walls; only the numerical coefficients have changed.

V. Discussion

The calculations presented above give the average length and number of bridges for polymers between two parallel plates, first for a single ideal long chain and then for semidilute polymer solutions. The two fundamental lengths we have calculated are the average spacing between bridges $\tilde{N}$ and the average length of the bridges $\bar{N}$. Here we will summarize and interpret these results by using a blob picture; then we will discuss the contribution of bridging to the forces between surfaces immersed in polymer solutions, with emphasis on the nonequilibrium effects associated with rapid separation of the surfaces.

(1) A Summary of the Results and the Blob Picture. All of the results for $\tilde{N}$ and $\bar{N}$ derived above can readily be obtained (up to numerical factors of order unity) and understood within a blob picture of the sort originally introduced by de Gennes[12] to understand polymer configurations. The chain is viewed as a sequence of "blobs", whose size is chosen to be one of the relevant physical lengths characterizing the polymer configuration, so that the behavior within each blob is simple. If there are additional important length scales, then the smaller are consolidated into larger blobs on the new scale. Let us then recall the results obtained above for the bridging lengths in various regimes and interpret each in terms of a suitable picture of this type.

For the single ideal long chain we have considered the limits of weak and strong attraction to the surfaces. In the weak attraction limit $\tilde{N}$ and $\bar{N}$ were found to be (eq III.7 and III.9)

$$\tilde{N} \sim (h/a)^2; \quad \bar{N} \sim (h/a)^2 - (h/a) \tag{V.1}$$

where $2h$ is the separation between the plates and a is the monomer size. The only relevant length in the problem is the confinement distance $2h$, and we view the chain in terms of blobs of this size. Within each one the effects of the plates are weak, and therefore the chain is Gaussian within such a blob, which contains of order $(h/a)^2$ monomers. The result for $\tilde{N}$ in eq V.1 is consistent with this picture, which implies that on the average there is of order one bridge per blob. Since $h \gg a$, the result (V.1) for $\bar{N}$ is also readily understood within this picture. The fraction of monomers within a single blob that are in contact with either bounding surface is of order the ratio of the surface layer thickness a to the blob diameter $2h$, since the monomer distribution between the plates is spatially uniform. Then the *number* of monomers in contact with the surfaces is of order $(a/h)(h/a)^2 = h/a$. The remaining monomers in the blob (the overwhelming majority, since $(a/h) \ll 1$) are left to form the bridge (or few bridges), their number $\bar{N}$ then being approximately $(h/a)^2$ reduced by those ($\sim h/a$ in number) in contact with the surfaces, as given by the result (V.1). This picture also enables us to speculate on the problem of chains with excluded volume interactions, in which case each chain within a blob becomes a Flory chain, where the number of monomers and the size are related by $h \sim \tilde{N}^{3/5}a$. Thus

$$\tilde{N} \sim \bar{N} \sim (h/a)^{5/3} \tag{V.2}$$

The bridging lengths are shorter in this case because of the swelling of the chain in the presence of excluded volume repulsion.

If the attraction of the surfaces is strong ($\kappa h \gg 1$), we have found (eq III.12 and III.21)

$$\tilde{N} \sim \left(\frac{D}{a}\right)^2 e^{h/D}; \quad \bar{N} \sim \left(\frac{D}{a}\right)^2 \frac{h}{D} \tag{V.3}$$

These results may also be understood from a blob picture. The size of the blob is now set by the characteristic length D of the attraction to the surface, so that within each one the effects of the surfaces are weak. The number g of monomers per blob is then $g \sim (D/a)^2$ in the case of ideal chains and $g \sim (D/a)^{5/3}$ for excluded volume chains. Each configuration can be viewed in terms of free diffusion (random walk) of a blob between two parallel plates. Due to the attraction to the surfaces, the energy of the blob is lower on the surfaces than it is between them. The difference is of order $\Delta\epsilon \sim T$, since there are $\sim D/a$ monomers per blob in contact with the surface, and each monomer contributes a potential energy of order $-(a/D)T$. Consider the diffusion of a blob starting from one surface. Due to the lower potential energy, it is favorable for it to stay on the surface. The relative probability for it to diffuse one step into the middle rather than along the surface is given by the Boltzmann factor $e^{-\Delta\epsilon/T} \approx e^{-1}$. Similarly, the probability for the blob to diffuse n steps into the middle rather than along the surface is $e^{-n\Delta\epsilon/T} \approx e^{-n}$. Since the minimum number of steps for the blob to diffuse from one surface to another is h/D, on the average there is one bridge formed by h/D blobs for each section of the chain of length $e^{h/D}$ blobs, as suggested by the result (V.3). Again this physical picture enables us to speculate on the extension of these results to chains with excluded volume interactions. We have, in general

$$\tilde{N} \sim \left(\frac{D}{a}\right)^{\upsilon} e^{h/D}; \quad \bar{N} \sim \left(\frac{D}{a}\right)^{\upsilon} \frac{h}{D} \tag{V.4}$$

where $\upsilon = 2$ for ideal chains and $\upsilon = {}^5/_3$ for excluded volume chains.

For bridging in semidilute polymer solutions, we find that the solutions for $\tilde{N}$ and $\bar{N}$ have features similar to the corresponding quantities in the single chain problem. The blob picture remains useful for understanding these results in a qualitative way, but we must in general account for the new size scale introduced by the correlation length ξ. In the simple case that the attraction to the surfaces is so weak that D is even larger than the plate separation $2h$, then D does not enter the picture. The fundamental blobs of size ξ contain $(\xi/a)^2$ monomers each. The configurations are those of the single chain between noninterative surfaces, but with the monomers replaced by these blobs. This leads to the results $\tilde{N} \sim \bar{N} \sim (\xi/a)^2(h/\xi)^2 = (h/a)^2$, unaffected by the excluded volume interactions (as we would expect for this situation, where the polymer density will be constant throughout the confined volume). When $h > D > \xi$, there is attraction from the walls, but the strength of the attraction is still weaker than the excluded volume interactions between monomers. Then the fundamental blobs of size ξ consolidate into larger ones of size D, and since the latter sets the scale of spatial variation imposed on the system here, the configurations within even the larger blobs can be taken to be the constant potential ones (random walk, within mean field theory). Again the functional dependences for $\tilde{N}$ and $\bar{N}$ are those of the single chain, here with $h > D$. The correlation length ξ does not enter within simple mean field theory, where the configurations both within the elementary blob of size ξ and for those blobs on the larger length scale D are given in terms of random walks. This will no longer be the case when the elementary blob is described more accurately—

for example, in terms of Flory chains. When the attraction of the walls becomes stronger than the excluded volume interactions, the repulsion between monomers plays an important role in bridging. As is usual in cases where there are two important length scales, we are unable to make unambiguous a priori predictions from the blob picture. However, we can interpret the calculated results of the last section within that picture. We see from the result (IV.18), $\bar{N} \sim (h/\xi)(\xi/a)^2$, that on the average each bridge corresponds to a straight path between the two surfaces formed by h/ξ blobs of size ξ. The number of monomers between successive bridges was found (eq IV.15) to be $\tilde{N} \sim (\xi/D)(\xi/a)^2 e^{h/\xi}$. The exponential is believed to have an origin similar to that described in the diffusing blob picture above, and $(\xi/a)^2$ corresponds to the number of monomers per blob. The factor of ξ/D reflects the strong attraction effect within a distance, D, of the surfaces.

Our mean field model neglects screening effects from the excluded volume interactions. However, the blob picture allows us, as before, to make reasonable qualitative speculations about these effects. For example, in the case of a semidilute solution between two noninteractive surfaces, a bridge will still be viewed as a random walk of blobs of size ξ between the two surfaces, but the number of monomers within that blob will be related to its size by the exponent $\upsilon \approx {}^5/_3$ rather than the mean field value of 2, due to screening. Thus, we have $\tilde{N} \sim \bar{N} \sim (h/\xi)^2(\xi/a)^{5/3} = (h/a)^2(a/\xi)^{1/3}$. The bridging lengths are then reduced in the presence of screening.

(2) Bridging and Attraction between Surfaces. We now discuss some important implications of our calculations for the forces between surfaces in polymer solutions due to bridging.

(a) The Onset of Bridging Attraction. If two plates immersed in a polymer solution are brought close to one another adiabatically, so that the adsorbed layers are maintained in full equilibrium with the ambient solution, attraction will be observed below a maximum separation between the plates. It has been suggested[2-4] that this attractive force is due to polymer bridges; the separation h^* at which bridges first form should then signal the onset of attraction. For polymer chains with molecular weight N, bridges start to form between the two surfaces at the separation where the length between bridges $\tilde{N}(h)$, determined by the minimization of the free energy as discussed above, approaches N (in general, a substantially smaller separation than the length of a stretched chain Na, where it is first geometrically possible to establish a bridge). In the limit of strong wall–monomer attraction ($\kappa\xi \gg 1$), this gives for h^*

$$N \sim \kappa\xi\left(\frac{\xi}{a}\right)^{5/3} e^{h^*/\xi} \qquad \text{(V.5)}$$

which implies that

$$h^* \sim \xi \ln\left[N\frac{a^{5/3}}{\kappa\xi^{5/3}}\right] \qquad \text{(V.6)}$$

This gives us an estimate of the range h^* of the bridging attraction. It predicts that this range strongly depends on the bulk correlation length ξ and that it is proportional to the logarithm of the molecular weight N. The adsorption energy set by κ, on the other hand, does *not* affect this interaction range substantially. These predictions agree with the numerical results of Scheutjens and Fleer[1] except for one feature: those authors predicted for h^* only a weak dependence on the bulk concentration Φ_b, in contradiction with our result (V.6), since the correlation length ξ, which appears important, is proportional to the inverse square root of Φ_b. It would clearly be illuminating to have experimental studies of this dependence.

(b) Nonequilibrium Attraction Hysteresis. When the two plates are pulled apart sufficiently rapidly, bonds with the surface do not have time to break and re-establish themselves in equilibrium at the new separation. As a consequence the attraction between the plates provided by the bridges will be greater than that observed at equilibrium at the larger separation. Consider a simple example of a single chain between two plates. The number of bridges is $N/\tilde{N}$, where N is the molecular weight of the chain. In the limit of strong wall–monomer attraction, each bridge is in a strongly stretched state—i.e., the number of monomers on one bridge $\bar{N}$ is much less than the number in a free chain of the same linear dimension h (see eq V.4). For one bridge in such a stretched state, the equilibrium tensile force is not of the form of Hooke's law (proportional to h); rather, it is given by[12]

$$\frac{F_0(h)a}{T} \sim \left(\frac{h}{\bar{N}a}\right)^{3/2} \qquad \text{(V.7)}$$

Using this equation and eq V.4 for $\bar{N}$ and $\tilde{N}$, we find that for one excluded volume chain between two plates, the bridging attraction is

$$\frac{F(h)a}{T} = \frac{N}{\tilde{N}}\frac{F_0(h)a}{T} \sim N\left(\frac{a}{D}\right)^{19/9} e^{-h/D} \qquad \text{(V.8)}$$

Just such an exponential dependence of the attractive force on plate separation h has been observed[13] in dilute polymer solutions.

Now consider pulling apart the plates, increasing their spacing from h to h_1, sufficiently quickly that bonds are neither broken nor established. By definition neither $\tilde{N}$ and $\bar{N}$ changes, and the explicit dependence of the force $F_0(h_1)$ on the spacing is still given by (V.7). Then we have the simple relation that the (nonequilibrium) force between the plates at the larger separation is

$$F(h_1) = \left(\frac{h_1}{h}\right)^{3/2} F(h) \qquad \text{(V.9)}$$

We can carry out a similar calculation for the bridging force within a semidilute polymer solution, using the results obtained above for the relevant lengths $\bar{N}$ and $\tilde{N}$. For the equilibrium attraction in the limit $h > \xi > D$ we find that eq V.8 is replaced by

$$\frac{f(h)a}{T} \sim n_b F_0(h)a/T \sim h\Phi_b(1 + \xi^2/hD)\frac{Da^2}{\xi^3}e^{-h/\xi} \qquad \text{(V.10)}$$

where $n_b = n_m/\tilde{N}$ is the number of bridges per unit area of boundary surface ($n_m \sim h\Phi_b(1 + \xi^2/hD)$ is the corresponding density of monomers in solution), and we have now necessarily calculated the total attractive force per unit area rather than the force due to a single chain. The dominant dependence on plate separation h is again exponential. By the same reasoning used above we conclude that the nonequilibrium attraction associated with rapid separation of the plates scales with the ratio of new to old separation h_1/h to the 3/2 power, as given by eq V.9.

We urge further experimental investigation of the behavior we have predicted here for the forces between parallel plates in polymer solution.

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Photochromism of Liquid-Crystal Polyacrylates Containing Spiropyran Groups

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ABSTRACT: Acrylic copolymers with mesogenic and spiropyran side chains yield a photochromic mesophase absorbing strongly in the visible region (λ_{max} 570–590 nm) on irradiation with UV light. The color disappears on irradiation with visible light or thermally. Thermodynamic spectroscopic and kinetic properties of the photochromic polymers were investigated. The structure of the mesophase is discussed.

Introduction

Incorporation of photo- and thermochromic spiropyrans side groups in polyvinyl macromolecules leads to substantial changes in the polymer structure stemming mainly from interactions between these side groups in their colored merocyanine form.[1–5] Conversion of spiropyran into merocyanine dye can be induced by UV irradiation, by heating of the polymer or by swelling of the polymer in a polar solvent. The dipolar and highly polarizable merocyanine groups have a very strong tendency to dimerization and further aggregation, which occurs both in solution and in bulk. The aggregation proceeds most efficiently on swelling or on heating the polymer above the glass transition temperature (T_g) when the segmental mobility of macromolecules is high enough to promote the dye aggregation, while irradiation below T_g produces mostly isolated dye molecules. At a high content of spiropyran groups in a copolymer, the aggregation may reach a degree at which the aggregates can be observed in an electron or even an optical microscope.[4] Moreover, swelling of a homopolymer containing only spiropyran units results in crystallization of the polymer by virtue of solvatochromic spiropyran–merocyanine conversion followed by self-assembly of the merocyanine groups into a three-dimensional crystalline lattice (so-called zipper-crystallization). The resulting polymer gave discrete Debye–Scherrer diffraction patterns and a degree of crystallinity of up to 40%.[1,3]

The absorption spectra and kinetic properties of the photochromic polymers are also strongly affected by aggregation. A hypsochromic shift of the visible band was observed when separated mercyanine groups form dimers or higher aggregates. The aggregates belong to the so-called H-type, which is characterized by antiparallel dipole–dipole interactions of molecules. The absorption bands of monomeric merocyanine molecules and aggregates usually overlap. However, important conclusions about the degree of aggregation can be drawn from the absorption band shift and the kinetics of the spontaneous merocyanine–spiropyran back-reaction.[2,6] For example, for many indoline–spiropyrans the visible absorption maximum was found to shift from ~580–590 to ~560 nm, and in thermal decoloration rate, to decrease about 5-fold when passing from isolated mercyanine molecules to dimers.[2,6]

Recently,[7–9] we reported thermochromic properties of liquid-crystal polyacrylic copolymers containing mesogenic and spiropyran side groups (Scheme I). Films of these mesomorphic copolymers change color on heating. At room temperature the electronic absorption bands of the films in the visible region lie in the range 460–600 nm, which is characteristic of merocyanine dyes both in the aggregated and nonaggregated form. Absorption bands with $\lambda_{max} \leq 560$ nm have been again ascribed to dimers and higher merocyanine aggregates, while the bands with $\lambda_{max} \geq 570$ nm belong apparently to nonaggregated merocyanines. The merocyanine aggregation leads to cross-linking of the macromolecules and network formation. A direct proof of such a physical cross-linking of the macromolecules was obtained by measurements of the copolymer melt viscosity as a function of temperature and spiropyran content.[7,8]

Similar properties were observed in liquid-crystal side-chain polysiloxanes containing spiropyran groups.[9,10] In

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