

Polymer-Induced Wetting Transitions in Liquid Films

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ABSTRACT: Using the single chain mean field (SCMF) theory we investigate the effect of soluble polymer chains on the surface tension between a solid surface and liquid films. We find that end-grafted chains (brush) strongly reduce the surface tension between a liquid and an incompatible solid. This reduction is insensitive to the type and strength of monomer–solid interactions. Free chains reduce the surface tension between the liquid and the solid only if the monomer–solid interaction is attractive. Combining free and densely end-grafted chains is found to *inhibit* wetting, due to an inherent incompatibility between the grafted polymer brush and the free chain solution. Combining free and moderately end-grafted chains is found to *enhance* wetting if the monomer–surface interactions are attractive. These predictions are in good agreement with the experiments of Yerushalmi-Rozen et al.

I. Introduction

Interfacial properties strongly affect the characteristics and performance of materials. The ability to control surfaces is, therefore, of significant scientific and technological interest. One method by which surface parameters may be modified without affecting bulk moduli is through the application of thin surface coatings. To be effective, such coatings must provide uniform, stable coverage. Yet, in most cases the coating film is incompatible with the surface and dewets, i.e., breaks into isolated droplets.

Inducing wetting in incompatible surface–liquid films is a challenge. A common way of enhancing compatibility is by use of surface-active agents. Such molecules are designed to contain groups that are soluble in, or compatible with, both media. Thus, they aggregate at the interface and reduce the interfacial tension, similarly to the way surfactants reduce the interfacial tension between oil and water.

Monolayers of small molecule surfactants are effective in converting a hydrophobic surface into a hydrophilic one, and vice versa. However, wetting depends on more than the surface hydrophobicity; long range interactions (e.g., van der Waals) also play a significant role.¹ Polymers, on the other hand, make ideal surface modifiers due to their versatility, diversity, and availability. To reduce the surface tension between the liquid and the solid surface, the polymeric additive contains groups that are compatible with both. Unlike the small molecule amphiphiles, which are effective as wetting inducers only in hydrophobic–hydrophilic systems, polymers can be synthesized to induce wetting for various types of incompatibility. Moreover, the thickness of polymer surface layers can be controlled through the chain molecular weight, which allows production of surface layers that are an order of magnitude, or more thicker than the surfactant layers.²

The effect of polymeric surface layers on the spreading of small molecule liquids (i.e., solvents) or semidilute

polymer solutions is of significant technological importance in the field of coatings. Wetting of polymeric films by small molecule solvents is also of significant scientific interest, since, as will be discussed presently, the phenomena is not well-understood.² However, most studies focus on the effect of polymer surface layers on the wetting of polymeric *melts* (see, for example refs 3–8). While this problem is of interest, it cannot shed light on the phenomena of polymer layer wetting by small molecule solvents, due to the qualitative and quantitative differences between the two types of liquids.

Several models examined the effect of polymeric surface layers on the spreading of small molecule liquids.^{9–13} Despite large differences in approach and methodology, they all focus on the role of chain entropy (which favors dewetting and the formation of thick films) vs monomer–surface interactions (which may favor thin films with large contact area in the case of attractive surface–monomer interactions or thick, non-wetting films if those are repulsive). As a result, the models predict that solutions containing polymers whose monomers have an unfavorable interaction with the surface would dewet more strongly than the pure solvent, even if the chains are attached by one end to the surface so as to form a brush.^{9–13} Wetting may be enhanced, however, if the interactions between the monomers and the surface are attractive¹³ (Marques, C. M.; Shim, D. F. K.; Brooks, J. T. private communication).

Few experimental studies explore the effect of polymeric additives on wetting of surfaces by low molecular weight liquids.² The findings of Yerushalmi-Rozen et al. seem to support most of the theoretical predictions: Dewetting is not affected by the addition of polymers that do not interact favorably with the surface (i.e., they do not adsorb)^{14–16} or by attaching such polymers by one end to the surface.^{14–16} It should be noted, however, that the end-grafted surface layer traps a solvent layer whose thickness is similar to that of the polymer one, in agreement with model predictions.^{11,12} However, excess liquid dewets this solvated polymer film, as sketched in Figure 1.

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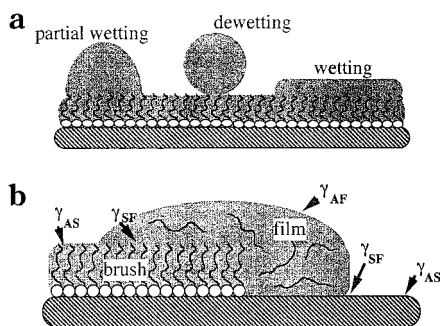


Figure 1. (a) The difference between wetting, dewetting, and partial wetting of thin liquid films spreading on brush-covered surfaces. In all cases we assume that the brush remains solvated,^{11,12} namely, traps a liquid layer whose thickness is equal to the chain dimensions. However, in the case of wetting, the film spreads to cover the entire surface. In the case of dewetting, the film forms spherical droplets to minimize the area of contact between the liquid and the brush surface. In the case of partial wetting, the film forms drops of a finite contact area and angle. (b) Surface tensions in the brush-liquid system. Since we define the surface as the combination of the solid support and the brush, γ_{AS} is the surface tension between the bare solid and air, if σ , the brush density, is zero, or the surface tension between the brush and air. Similarly, γ_{SF} may define either the solid-film surface tension or the brush-film surface tension. γ_{AF} is the surface tension between the film and the air interface.

Combining end-grafted and free chains whose monomers do not interact favorably with the surface also leads to dewetting, except for the case where the density of the end-grafted polymer layer was low.^{14–16} Increasing the concentration of free (unattached) chains in the solvent spread on this type of layer led to a transition from dewetting to wetting, at concentrations that were on the order of the overlap concentration.

None of the available models^{9–12} can explain how combining free chains in solution with end-adsorbed ones induces wetting, regardless of the brush density and/or the free chain concentration. This failure indicates that our understanding of the effect of polymeric additives on the wetting of surfaces by solvent films is incomplete.

In this paper we use the single chain mean field theory developed by Szleifer et al.^{18,19} to examine the effect of free and grafted polymer chains on wetting in liquid films. We concentrate on systems that are similar to the experimentally examined ones,^{14–16} where both grafted and free chains have the same chemical composition (e.g., PS free chains and an end-grafted PS brush) and molecular weight. Parameters include the type and strength of interaction between the chain monomers and the surface, the free chain concentration, and the brush density. The model allows us to calculate the different surface tensions (solid-film, brush-film, film-air) and, thus, not only evaluate wetting transitions but explore their origin.

We find that free chains enhance wetting only if the monomer-solvent interactions are attractive, in agreement with previous analysis.^{9,10} End-grafted chains are found to strongly enhance the compatibility between the surface and the pure solvent, regardless of the sign and strength of the specific monomer-surface interactions. We also show that wetting is not enhanced when free chains are combined with a high density, end-grafted brush. In fact, we find that the presence of free chains in solution strongly *reduces* the compatibility between the brush-covered surface and the free chain solution.

Thus, a pure liquid that does wet a brush can undergo a transition to partial wetting or dewetting when the concentration of free chains exceeds a critical value. However, in systems where the brush density is moderate (as, indeed, brushes in most experiments are) we find that adding free chains with an attractive affinity to the surface may *enhance* wetting. These results are in excellent agreement with the experiments of Yerushalmi-Rozen et al.^{14–16}

II. SCMF Theory

A dewetting film is defined as a film forming a droplet of zero contact area and infinite thickness. A wetting film forms a coating of zero thickness and infinite area. Partial wetting indicates the intermediate case, where the liquid drops are characterized by a given contact angle. The energy, per unit area, of a (bare) surface in contact with air, or vapor, is given by γ_{AS} . Similarly, γ_{SF} and γ_{AF} denote the energy, per unit area, of a surface interacting with a liquid film, and the film interacting with the air interface, respectively. Thus, neglecting long-range interactions (e.g., van der Waals), if¹

$$\gamma_{AS} \geq \gamma_{SF} + \gamma_{AF} \quad (1)$$

the film wets. If

$$\gamma_{AS} \leq \gamma_{SF} - \gamma_{AF} \quad (2)$$

the film will dewet. In intermediate cases where the film will partially wet the contact angle θ of the drops is given by Young's equation¹

$$\cos(\theta) = (\gamma_{AS} - \gamma_{SF})/\gamma_{AF} \quad (3)$$

We consider a system composed of N_g chain molecules of length n_g grafted to a planar infinite surface, in contact with a solution of free chain molecules of length n_f in a low molecular weight solvent. The solvent is a moderate (athermal) solvent for both grafted and free chains. Monomers are assumed to be identical, regardless of whether they belong to a grafted or free chain, and their volume is taken to be identical to that of a solvent molecule. The tethered molecules are characterized by their grafting density $\sigma = N_g/A$, where A is the surface area. The solution is characterized by the chemical potential of the free chains, μ_f , and the chemical potential of the solvent, μ_s . Our system is thus represented in a semigrand canonical ensemble, in the sense that the grafting density and the chemical potential of the free chains and solvent molecules are fixed. This is equivalent to the assumption that the solution is in contact with a reservoir of free chain and solvent molecules of a given concentration. Therefore, the relevant thermodynamic potential, or free energy, can be written as

$$\Omega = E - TS - \mu_f N_f - \mu_s N_s \quad (4)$$

where E is the internal energy, T is the temperature, S is the entropy of the system, and $N_s = \int_0^\infty N_s(z) dz$ and $N_f = \int_0^\infty N_f(z) dz$ are the total number of solvent and free chains, respectively.

SCMF theory was originally developed to study short surfactant aggregates^{20,21} and later generalized to treat tethered polymer molecules in contact with solvent.^{18,19} This theory is based on exact accounting of intramolecular interactions and on a mean field description of

intermolecular interactions. Surface interactions and any other interaction that depends on the coordinates of a single molecule are also included exactly. Therefore, the main quantities in the theory are the probability distribution function (pdf) of chain conformations.

The prediction of the theory for grafted polymer layers has been shown to be in quantitative agreement with experimental observations²² and computer simulations²⁵ for both structural and thermodynamic properties. The theory was also applied to study the adsorption behavior of proteins on surfaces covered by end-grafted polymer chains.^{23,24} The latter is analogous to our system of free chains in solution interacting with a surface covered by end-grafted chains, since in both cases two different pdfs must be examined, corresponding to the two different macromolecular species (free and surface-attached).

For simplicity, we apply the SCMF to our system in discretized space, so as to correspond to the implementation of the theory in computer code. Therefore, we divide the system into layers of thickness (δ) parallel to the grafting surface. The free energy (per unit area) of the system is written as

$$\beta\Omega = \frac{1}{A} \left[N_g \sum_{\{\alpha_g\}} P(\alpha_g) \ln P(\alpha_g) + \sum_{j=1}^M N_f(j) \sum_{\{\alpha_f\}} P(\alpha_f, j) \times \right. \\ \ln P(\alpha_f, j) + \sum_{j=1}^M N_f(j) \ln \frac{N_f(j)v_0}{A\delta} + \sum_{j=1}^M N_s(j) \ln \frac{N_s(j)v_0}{A\delta} + \\ \left. N_g \sum_{\{\alpha_g\}} P(\alpha_g) \sum_{i=1}^M \beta\chi_s(i) n_g(i, \alpha_g) + \sum_{j=1}^M N_f(j) \sum_{i=1}^M P(\alpha_f, j) \times \right. \\ \left. \beta\chi_s(i) n_f(i, j, \alpha_f) - \beta\mu_f \sum_{j=1}^M N_f(j) - \beta\mu_s \sum_{j=1}^M N_s(j) \right] \quad (5)$$

The first two terms correspond to the conformational entropy of grafted and free chains, respectively. $P(\alpha_g)$ is the probability of finding a grafted chain in conformation α_g . $P(\alpha_f, j)$ is the probability of finding a free chain in conformation α_f at position j from the surface. By “position of the chain” we mean the coordinate of any point along the chain (for example, a chain’s end or the chain’s center of mass). The third and fourth terms in eq 5 are the translational entropy of the free chains and solvent molecules, respectively. $N_f(j)$ ($N_s(j)$) is the average number of free chains (solvent molecules) in layer j . The fifth and sixth terms of the free energy correspond to the monomer–surface interaction for grafted and free chains, respectively. This interaction is described by a potential $\chi_s(i)$. $n_g(i, \alpha_g)$ is the number of segments that a grafted chain in conformation α_g has in layer i , and $n_f(i, j, \alpha_f)$ has a similar meaning for a free chain characterized by its position j in conformation α_f . Finally, the two last terms impose constant chemical potentials for both the free chains (μ_f) and solvent molecules (μ_s) through the layer. The upper limit for the number of layers, M , is chosen so as to ensure that the bulk limit has been reached. If M_g is the furthest layer from the surface that the grafted chains can reach and M_f is the maximum number of layers that a free chain can occupy, then $M = M_g + 2M_f$ is sufficient. Larger M will produce an additive constant to the free energy with no physical consequences.

We assume system incompressibility. Therefore, any arbitrary volume (layer) is completely filled with chain monomers and/or solvent molecules. Using the symmetry of our problem we express this incompressibility

constraint for the layer i as

$$N_g \sum_{\{\alpha_g\}} P(\alpha_g) n_g(i, \alpha_g) v_0 + \sum_{j=1}^M N_f(j) \sum_{\{\alpha_f\}} P(\alpha_f, j) \times \\ n_f(i, j, \alpha_f) v_0 + N_s(i) v_0 = A\delta \quad (6)$$

Next, we minimize the system’s free energy (eq 5) subject to the volume filling constraint (eq 6) by introducing a set of Lagrange multipliers, $\beta\pi(i)$. There are as many Lagrange multipliers as number of layers. The role of the volume-filling constraint is to effectively introduce intermolecular repulsion in the problem. As a result of the minimization we obtain (a) the pdf of the grafted chain’s conformations

$$P(\alpha_g) = \frac{1}{q_g} \exp \left[- \sum_{i=1}^M \beta\pi(i) v_0 n_g(i, \alpha_g) - \sum_{i=1}^M \beta\chi_s(i) n_g(i, \alpha_g) \right] \quad (7)$$

where $q_g = \sum_{\{\alpha_g\}} P(\alpha_g)$ normalize the pdf, (b) the pdf for the free chains

$$P(\alpha_f, j) = \frac{1}{q_f(j)} \exp \left[- \sum_{i=1}^M \beta\pi(i) v_0 n_f(i, j, \alpha_f) - \sum_{i=1}^M \beta\chi_s(i) n_f(i, j, \alpha_f) \right] \quad (8)$$

with $q_f(j) = \sum_{\{\alpha_f\}} P(\alpha_f, j)$, (c) the number of free chains per unit area, and

$$\frac{N_f(j)}{A} = \frac{\delta}{v_0} q_f(j) e^{\beta\mu_f - 1} \quad (9)$$

(d) the solvent volume fraction

$$\phi_s(i) = \frac{N_s(i)v_0}{A\delta} = e^{\beta\mu_s - 1} e^{-\beta\pi(i)v_0} \quad (10)$$

This last equation demonstrates the physical meaning of the Lagrange multipliers $\beta\pi(i)$: The chemical potential of the solvent turns out to be $\beta\mu_s = 1 + \ln \phi_s(i) + \beta\pi(i)v_0$; then $\pi(i)$ is the osmotic pressure in the i th layer necessary to keep the chemical potential constant throughout the system. The actual value of μ_s is not relevant in this problem and we will set it to be $\beta\mu_s = 1$.²⁶ Thus, pure solvent conditions are represented by $\pi = 0$.

Results are obtained by solving a system of nonlinear equations for the pressures $\pi(i)$:

$$\frac{v_0}{\delta} \sum_{\{\alpha_g\}} \exp \left[- \sum_{i=1}^M \beta\pi(i) v_0 n_g(i, \alpha_g) - \sum_{i=1}^M \beta\chi_s(i) \times \right. \\ \left. n_g(i, \alpha_g) \right] n_g(i, \alpha_g) + e^{\beta\mu_f - 1} \times \\ \sum_j \sum_{\{\alpha_f\}} \exp \left[- \sum_{i=1}^M \beta\pi(i) v_0 n_f(i, j, \alpha_f) - \sum_{i=1}^M \beta\chi_s(i) \times \right. \\ \left. n_f(i, j, \alpha_f) \right] n_f(i, j, \alpha_f) + e^{-\beta\pi(i)v_0} = 1$$

The input for these equations are the grafting density, σ ; the chemical potential (or bulk concentration) of the free chains, μ_f ; and a set of single chain conformations for the grafted and free polymers, $\{\alpha_g\}$ and $\{\alpha_f\}$, respectively.

Once we know the $\pi(i)$ we can calculate the system's free energy per unit area

$$\beta\Omega = -\sum_{i=1}^M \beta\pi(i)\delta - \sigma \ln q_g - \sum_{i=1}^M \frac{\delta}{v_0} q_f(i) e^{\beta\mu_f - 1} - \sum_{i=1}^M \frac{\delta}{v_0} e^{-\beta\pi(i)v_0} \quad (11)$$

Any thermodynamic property can be derived from this expression. The surface tension is²⁷

$$\begin{aligned} \beta\gamma &= \left(\frac{\partial A\beta\Omega}{\partial A} \right)_{T,V,N_g,\mu_s,\mu_f} \\ &= -\sum_{i=1}^M \beta[\pi(i) - \pi_{\text{bulk}}]\delta - \sum_{i=1}^M \frac{\delta}{v_0} [q_f(i) - q_{f,\text{bulk}}] e^{\beta\mu_f - 1} - \sum_{i=1}^M \frac{\delta}{v_0} [e^{-\beta\pi(i)v_0} - e^{-\beta\pi_{\text{bulk}}v_0}] \quad (12) \end{aligned}$$

where π_{bulk} and $q_{f,\text{bulk}}$ are the values of the lateral pressure and the single chain partition function for the free molecules in bulk conditions. To calculate these values let us consider eq 6–10 under bulk conditions, namely, at a distance from the surface where the system is homogeneous. The pdf for the free chains reduces to

$$P(\alpha_f) = \frac{1}{q_{f,\text{bulk}}} e^{\beta\pi_{\text{bulk}}v_0 n_f} \quad (13)$$

and the solvent volume fraction is $e^{\beta\pi_{\text{bulk}}v_0}$. Then, the volume filling constraint (eq 6) gives one equation for π_{bulk}

$$Q_f e^{\mu_f - 1} e^{\beta\pi_{\text{bulk}}v_0 n_f} n_f + e^{\beta\pi_{\text{bulk}}v_0} = 1 \quad (14)$$

where Q_f is the number of elements in the set $\{\alpha_f\}$. Then, $q_{f,\text{bulk}} = Q_f e^{\beta\pi_{\text{bulk}}v_0 n_f}$.

The energies per unit area, or surface tensions, can be calculated by evaluating the effect of the different parameters on the lateral surface pressure at those interfaces. We need to emphasize that in our calculations the “surface” includes both the solid support and the end-grafted polymer brush.

Examining the definition of wetting (eqs 1–3), we see that for each system we need to calculate three parameters: γ_{AS} , the surface tension between the solid surface and the air (or vapor); γ_{AF} , the surface tension between the liquid–polymer solution and air (or vapor); and γ_{SF} , the surface tension between the brush-covered surface and the liquid–polymer solution.

In a system where a pure liquid drop is spread on a (bare) solid substrate, γ_{AS} , γ_{AF} , and γ_{SF} are all constants determined by the type of solid surface, liquid properties, and the air (or vapor) environment. We define these arbitrary constants as γ_{AS0} , γ_{AF0} , and γ_{SF0} . Since we have three arbitrary parameters, we can set one of them, γ_{AF0} , to be zero.

Adding free chains of a given molecular weight to the pure liquid drop will not affect, obviously, the value of

γ_{AS} , which will remain at γ_{AS0} . However, the values of γ_{AF} and γ_{SF} will vary, as a function of the monomer–interface interactions and the polymer chain concentration. Therefore, we may write $\gamma_{AF} = \gamma_{AF0} + \Delta\gamma_{AF}(\phi_b, \chi_a)$, where χ_a defines the monomer interaction with the air interface, and similarly, $\gamma_{SF} = \gamma_{SF0} + \Delta\gamma_{SF}(\phi_b, \chi_s)$. In the following discussion, we will assume that there is no enthalpic interaction of the monomers with the air interface, so that $\chi_a = 0$. However, we will still have a dependence of γ_{AF} on ϕ_b , due to the depletion interactions of chains near an uncrossable surface.

Covering the surface with an end-grafted brush would not affect γ_{AF} ; it will remain at its initial value, γ_{AF0} , since we assume that the brush does not extend to the air–liquid interface. However, our surface is defined by the combined brush–solid, so that γ_{AS} is affected by the presence of the brush. Yet, for a strongly stretched brush above, this dependence should be small.¹⁷ We assume, therefore, that $\gamma_{AS}(\sigma, \chi_s)$ is a constant, γ_{ASb} , where the notation b stands for the solvated brush.

Our system is therefore defined by three constants, γ_{AF0} , γ_{ASb} , and γ_{SF0} . The effect of the free chain concentration and/or the brush density on the different tensions will be calculated from the solution of the SCMF through evaluation of the different $\Delta\gamma$ terms.

III. Results

All the results shown in this section correspond to systems where both free and grafted chains ($n_g = n_f$) are 32 segments long. The chain segments are modeled as tangent hard spheres of diameter l . The thickness of the layers was chosen to be $\delta = 1.86l$, and $M = 50$ layers were considered. The free chain concentration is given in units of volume fraction, ϕ_b . The density of end-grafted chains is given by the dimensionless surface density, σl^2 , where $1/\sigma$ is the area per chain. The monomer–surface potential χ_s is a square well of range δ .

End-Grafted Chains. In this section we examine the effect of end-grafted chains on the surface tension between a (pure) liquid and a solid surface. Since the air–solid and the liquid–air tensions (γ_{AF} , γ_{AS}) are assumed to remain constant, as discussed above, the compatibility between the brush-covered surface and the liquid is set only by $\gamma_{SF} = \gamma_{SF0} + \Delta\gamma(\sigma)$ (for convenience, we will not use, from now on, the subscripts when discussing $\Delta\gamma$). If $\Delta\gamma$ increases as a function of σ , this will indicate a reduced compatibility between the liquid and the brush-covered surface.

In Figure 2 we show the effect of brush density on $\Delta\gamma$. We see that as the brush density, σ , increases, the surface tension, γ_{SF} , decreases significantly. The sign and magnitude of the monomer–surface interaction do not affect this trend and, in fact, seem to have little quantitative effect as well. This is not surprising, since it has been shown that the effect of the monomer–surface interaction is limited to a narrow region near the surface and does not greatly affect the chain configuration in the brush's outer region.¹⁷

These results are in agreement with our expectation, that to induce wetting one must replace an incompatible surface (the solid) by a compatible one (the liquid-soluble chains). Increasing the brush density decreases the area of contact between the bare solid and the liquid and thus increases compatibility. Therefore, we predict that wetting may be induced in such systems if the brush grafting density is high enough. Note that, since our

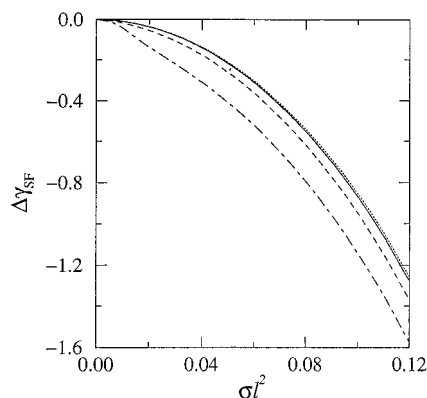


Figure 2. The effect of the brush density on the surface tension between a pure liquid ($\phi_b = 0$) and a brush-covered surface. $\Delta\gamma = \gamma_{SF}(\sigma) - \gamma_{SF}(\sigma = 0)$. We see that the surface tension between the liquid and the brush-covered surface decreases monotonically and significantly with increasing brush density. The solid line corresponds to $\beta\chi_s = 0$, the dotted line to $\beta\chi_s = 0.5$, the dashed line to $\beta\chi_s = -0.5$, and the dotted-dashed line to $\beta\chi_s = -1.0$. The chain molecular weight is 32. The overlap surface density for this molecular weight is $\sigma l^2 = 0.04$. Note: in the y-axis label we are using γ instead of the actual plotted quantity, the dimensionless $\beta\gamma l^2$.

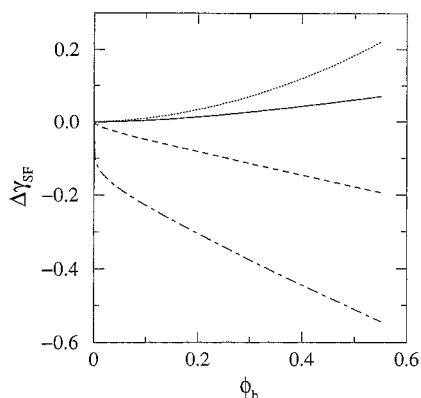


Figure 3. The effect of the free chain concentration on the surface tension between the solid surface and the solution. Here $\sigma = 0$ and $\Delta\gamma = \gamma_{SF}(\phi_b) - \gamma_{SF}(\phi_b = 0)$. The lines are as in Figure 2.

surface is defined as the solvated brush, “dewetting” indicates the formation of spherical droplets on top of the swollen brush, while wetting means the formation of a stable, thick, uniform liquid film covering the entire brush surface (see Figure 1).

Free Chains. In Figure 3 we examine the effect of free chain concentration on the surface tension between a thin film and a bare, solid surface (namely, $\sigma = 0$). As expected, we find that when the monomer–surface interaction is attractive ($\chi_s \leq 0$), $\Delta\gamma_{SF}$ decreases with ϕ_b , the free chain concentration. A repulsive interaction between the monomers and the bare surface has the opposite effect.

Figure 3 also displays the effect of free chain concentration on the film–air interface. Assuming that the air interface is flat and that there are no specific enthalpic interactions between the polymer monomers and air ($\chi_a = 0$), we indeed see that γ_{AF} increases slowly with the polymer concentration. This increase is due to the entropic depletion that chains encounter near an uncrossable interface.

Combining End-Grafted and Free Chains. In general, solutions of identical chains in the same, good solvent are highly compatible. Thus, one might expect

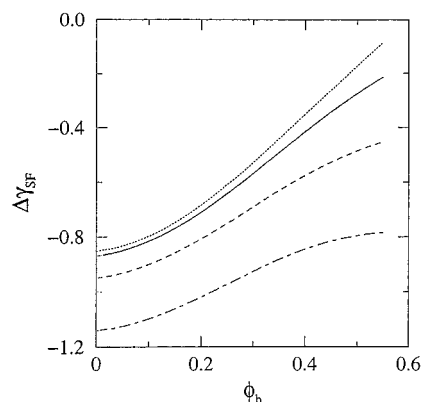


Figure 4. The effect of combining free chains and end-grafted chains (brush) on γ_{SF} , for a brush density $\sigma l^2 = 0.1$. As in Figure 2, $\Delta\gamma = \gamma_{SF}(\phi_b) - \gamma_{SF}(\phi_b = 0)$. The surface tension between the brush and the free chain containing film increases, regardless of the sign of χ_s . The lines are as in Figure 2.

that a solution of free chains will be highly compatible and spread on a similar solution composed of end-grafted chains on a surface. However, we find that (Figure 4) combining densely end-grafted chains in a brush with free chains in solution *increases* γ_{SF} for all solution concentrations and values of monomer–surface interactions.

Why does increasing the free chain concentration decrease the compatibility between the free chain solution and the brush-covered surface? The fact that the increase in γ_{SF} is insensitive to the type and sign of the monomer–surface interaction indicates that it is probably not due to the surface. Thus, we must conclude that the incompatibility arises from some unfavorable interaction between the free and grafted chains.

In Figure 5 we plot the density profiles of both free and brush chains, for different values of χ_s and ϕ_b . We see that in all cases the free chains do not penetrate deeply into the brush region. In fact, they do not reach the surface at all, which explains why χ_s does not affect the increase in brush–free chain solution surface interactions. As ϕ_b increases, the interpenetration region increases as well. More importantly, however, is the fact that the brush is compressed. This compression must be unfavorable, thereby leading us to the somewhat unexpected conclusion that the interactions between a free chain solution and a brush become *less* favorable as the concentration of free chains increases.

The results of our calculations for the high-density brush are summarized in Figure 6, where we plot the wetting phase diagram, as a function of the free chain concentration. We can imagine an experiment where we start with a pure liquid film at some value of γ_{AS0} that corresponds to the wetting regime (which is, in this case, greater than 0.25). Examining the wetting behavior of a solution of free chains, as a function of the free chain concentration, will therefore follow a horizontal line in this diagram. Adding free chains to the liquid slowly increases the value of γ_{SF} , as shown in Figure 4, until we crossover to the partial wetting regime. Further increase in ϕ_b will lead to a second crossover, to a dewetting regime. It should be noted that this behavior, namely, the succession of transitions from wetting to partial wetting to dewetting, as a function of increased free chain concentration, is not dependent on the (arbitrary) values we chose for γ_{AF0} and γ_{SF0} .

Thus, we see that adding free chains to a liquid does not improve wetting when the surface is covered by a

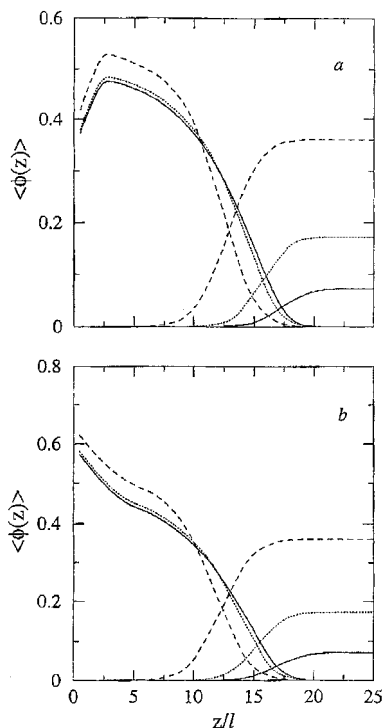


Figure 5. Density profiles of free and brush chains. z defines the distance from the solid surface, in units of the monomer size. The three film concentrations correspond to $\phi_b = 0.07$ (solid line), $\phi_b = 0.17$ (dotted line), and $\phi_b = 0.36$ (dashed line). $\sigma l^2 = 0.1$. In part a $\beta\chi_s = 0$, and in part b $\beta\chi_s = -0.5$. We see that in both cases increasing the free chain concentration increases the degree of brush chain compression. No free chains penetrate beyond the brush midpoint.

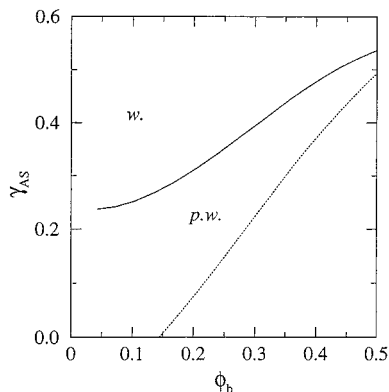


Figure 6. The wetting phase diagram for a free chain containing liquid spreading on a brush-covered surface where $\sigma l^2 = 0.1$ and $\beta\chi_s = -0.5$. As discussed in the text, the polymerless system is defined by three parameters: the surface tension between the bare surface and the air (or vapor), γ_{AS0} ; the surface tension between the pure liquid film and the bare surface, γ_{SF0} ; and the surface tension between the pure liquid and the air environment, γ_{AF0} . To obtain the phase diagram we (arbitrarily) set $\gamma_{SF0} = 1.0$ and $\gamma_{AF0} = 0.2$. The third parameter, γ_{AS0} , is given by the y axis. An experiment examining the spreading of a liquid film on a brush-covered surface, as a function of the free chain concentration, will follow a horizontal line in this diagram, the height of which will be set by the value of γ_{ASb} . (W) denotes the wetting regime, and (PW) the partial wetting regime.

high-density brush. In fact, increasing the free chain concentration clearly does not improve wetting, when compared to the pure liquid ($\phi_b = 0$) case. Indeed, the opposite occurs: As the free chain concentration increases, the film may undergo transitions from wetting to partial wetting to dewetting.

IV. Discussion

Examining the effect of end-grafted chains on the surface tension between a liquid and a solid surface, we find that irreversibly attaching the polymer chains by one end to the surface *reduces* the surface tension between a liquid film and a solid surface. Increasing the brush surface density increases the film–surface compatibility and reduces the surface tension, thus enhancing wetting. Although this result contradicts an earlier study,¹¹ it is reasonable and consistent with our understanding of the system; replacing the incompatible solid surface with an irreversibly attached, compatible polymer layer should enhance wetting. The surface tension between the spreading liquid and the polymer-covered surface will decrease as the polymer density (and thus, compatibility) increases.

The surface tension between the brush-covered surface and the liquid film is largely insensitive to the type and strength of the monomer–surface interactions. This is due to the fact that the effect of these interactions does not extend far beyond the brush's inner region.¹⁷

Contrary to the end-grafted chain case, the effect of the free chain concentration on the surface tension between a (bare) solid surface and a polymer solution is very sensitive to the monomer–surface interactions; an attractive interaction enhances wetting, while a depletion interaction favors dewetting, in agreement with previous models.^{9,10} This can be simply explained by the fact that wetting increases the contact area between the solution and the surface, while dewetting will reduce both the contact area and the number of interactions.

Combining free and end-grafted chains might have led to one of two scenarios. The first is one where the effects of the two types of chains (free and end-grafted) are simply additive. In this case, γ_{SF} will be equal to the sum of $\gamma_{SF}(\sigma, \phi_b = 0)$ and $\gamma_{SF}(\sigma = 0, \phi_b)$. Plotting the surface tension between the brush-covered surface and the polymer solution, as a function of the free chain concentration ϕ_b , will then follow the same trends as those observed for the pure liquid (Figure 3), except for the fact that the starting point at $\phi_b = 0$ will be set by the brush and pure-liquid value (from Figure 2).

The additive scenario is appropriate for systems where there are no interactions between the different components. However, in our system the free chains interact with the end-grafted brush. One may therefore argue that, as ϕ_b increases, the brush region and the free chain solution become more similar and, hence, more compatible. Moreover, interpenetration between the brush and the free chain solution increases with ϕ_b , which is expected to enhance wetting, regardless of χ_s .^{14,15} However, our calculation clearly shows that the combination of free and densely end-grafted chains always *increases* γ_{SF} (Figure 4) for all values of χ_s , in qualitative agreement with the predictions of Martin et al.¹² Our model allows us to explain why: The thickness of a brush in pure solvent is set by a balance between entropy (favoring less extended configurations of the chains) and enthalpy (favoring stretching to enhance monomer–solvent interactions). A perturbation from this equilibrium value costs energy. When free chains are added to the liquid film, their osmotic pressure compresses the brush (Figure 5), thereby increasing the brush free energy. Dewetting will minimize the area of brush–solution contact and thus the perturbed area. This is also in agreement with the

experiments of Yerushalmi-Rozen et al.^{14–16}, where they find that a solution containing free chains always dewets a surface covered by a dense brush of short chains (where σ is about 6 times the overlap density). Note that in Figure 5, 6 is about 5 times the overlap concentration.

Yet, so far we failed to explain the observed transition from partial wetting to wetting^{14–16} in the case of high molecular weight, end-grafted chains. This is due to the fact that the density of the brush, in this case, was relatively low: σ was about 1.5 the overlap density, which, translated to our units, means $\sigma l^2 \approx 0.05$.

In Figure 7a we show γ_{SF} as a function of ϕ_b for a grafted layer of a moderate density where $\sigma l^2 = 0.05$. We see that when the monomer–solid interaction is unfavorable, γ_{SF} increases with the free chain concentration, as it did in the case of the high-density brush. However, unlike the case where σ is high, γ_{SF} first increases and then decreases with free chain concentration when χ_s is attractive.

The latter behavior can be clearly understood when examining the density profile (Figure 7b). As discussed earlier, free chains cannot penetrate deeply into the brush when σ is high (Figure 5). The osmotic pressure of the free chain solution on the brush leads to an energetic penalty, manifested in decreasing compatibility between the brush and the free chain solution. However, when the brush density is low or moderate, we see (Figure 7b) that as the free chain concentration increases, some free chains can penetrate well into the brush regime and adsorb, when χ_s is favorable, at the solid interface. The ensuing gain in interaction energy compensates for the associated brush compression penalty and may lead to an overall reduction in γ_{SF} .

The wetting diagram of a surface carrying a moderate density brush is presented in Figure 7c. As in the high-density brush (Figure 6), there is a branch where, when ϕ_b exceeds a critical value, the film will undergo a dewetting transition. This transition is due to the penalty associated with brush compression by the free chain solution. However, the second branch in the moderate density brush case allows a wetting transition and is due to the enthalpic gain associated with free chain adsorption at the solid interface.

Thus, combining the two wetting diagrams we may now explain the experimental observations of Yerushalmi-Rozen et al.^{14–16} End-grafted chains alone or free chains alone (although their interaction with the surface is weakly attractive) cannot induce wetting. Films containing free chains always dewet or partially wet a high-density brush. However, films spreading on a low-density brush form a stable, wetting layer when ϕ_b exceeded a critical value.

It should be noted that, throughout this discussion, we neglected the effect of long-range interactions on wetting. In general, film stability depends not only on the different surface tensions (eqs 1 and 2) but also on the type and strength of long range forces. However, we do not expect such long-range interactions to qualitatively affect our results, but only to quantitatively shift the wetting transition.

Another issue is the effect of solvent quality: our calculations were conducted for polymer chains in a moderate solvent. This corresponds to the experimental system which was composed of polystyrene chains in oligostyrene solvent.^{14–16} Would similar results be expected for chains in good solvent?

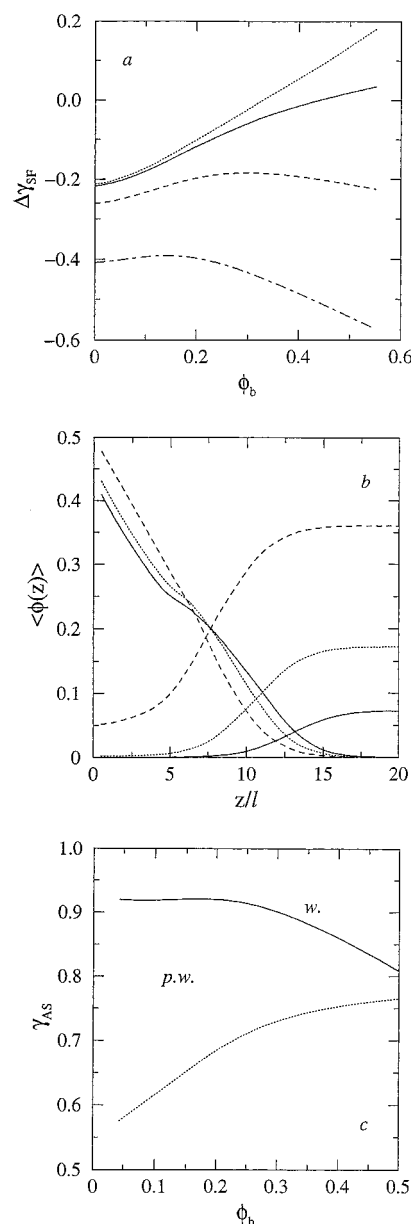


Figure 7. (a) The effect of combining free chains and end-grafted chains (brush) on the surface tension between a polymer-containing liquid film and a moderate density brush. $\sigma l^2 = 0.05$ and $N = 32$. We see that, when χ_s is negative, the surface tension first increases and then decreases to values below γ_{SF0} where $\phi_b = 0$. (b) Density profiles for free and end-grafted chains in the moderate density brush, $\sigma l^2 = 0.05$, $\beta\chi_s = -0.5$. The free chain concentrations are 0.07, 0.17, and 0.36. We see that brush compression by the free chains is moderate, and in the case of high ϕ_b , some free chains penetrate to the solid surface, thereby increasing the monomer concentration there. (c) The wetting phase diagram for moderate density brush. All parameters are as in part b and Figure 6. We see that, starting with a liquid that partially wets the brush, we may either undergo a transition to wetting or to dewetting, depending on the initial value of γ_{AS} .

Solvent quality affects several factors in the system. For example, the effective attraction between the monomers and the surface will decrease as the solvent quality increases. In fact, it is well-known that polymers that adsorb onto a surface from a poor or moderate solvent will desorb when solubilized in a good solvent. Thus, for a given polymer–surface system, increasing the solvent quality should lead to a reduction in χ_s . Also, the solvent quality affects the osmotic pressure between

the brush and the solution; in moderate solvents, the interactions between monomers are only somewhat less favorable than the interactions between the monomers and the solvent. As a result, the brush compression penalty is weak. In good solvent, this penalty will be much larger. Therefore, we expect that in good solvent polymer solutions will dewet brush-covered surfaces more readily than in a moderate solvent.

V. Conclusions

Using the SCMF theory we investigate the effect of free and/or end-grafted polymer chains on the surface tension of liquid films. We find that end-grafted chains strongly reduce the surface tension between a liquid and an incompatible solid. This reduction is independent of the type and strength of monomer–solid interactions. Free chains reduce the surface tension between a liquid film and a solid only if the monomer–solid interaction is attractive.

Combining free and end-grafted chains reduces, rather than enhances, wetting. We predict that a liquid that wets a brush-covered surface may undergo a transition to partial wetting or dewetting when the concentration of free chains exceeds a critical value. However, wetting may be obtained in these systems if two conditions are met: the brush density is moderate, and the interactions between the monomers and the solid surface are attractive. These results are in good agreement with the experiments of Yerushalmi-Rozen et al.^{14–16}

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References and Notes

- (1) See, for example: Leger, L.; Joanny, J. F. *Rep. Prog. Phys.* **1992**, 431–486.

- (2) Dan, N.; Yerushalmi-Rozen, R. *TRIP* **1997**, 5, 46–50.
- (3) Shull, K. R. *Macromolecules* **1996**, 29, 2659–2666.
- (4) Shull, K. R. *Macromolecules* **1996**, 29, 8487–8491.
- (5) Ferreira, P. G.; Ajdari, A.; Leibler, L. *Macromolecules* **1998**, 31, 3994–4003.
- (6) Yuan, C. G.; Meng, O. Y.; Koberstein, J. T. *Macromolecules* **1999**, 32, 2329–2333.
- (7) Jopp, J.; Yerushalmi-Rozen, R. *Macromolecules* **1999**, 32, 7269–7275.
- (8) Leibler, L.; Ajdari, A.; Mourran, A.; Coulon, G.; Chatenay, D. In *Ordering in Macromolecular Systems*; Teramoto, A., Norisuya, T., Eds.; Springer-Verlag: Berlin, 1994.
- (9) De Gennes, P. G. *Macromolecules* **1981**, 14, 1637–1644.
- (10) Boudoussier, M. *J. Phys. (Fr)* **1987**, 48, 445–455.
- (11) Johner, A.; Marques, C.M. *Phys. Rev. Lett.* **1992**, 69, 1827–1830.
- (12) Martin, J. I.; Wang, Z. G.; Schick, M. *Langmuir* **1996**, 12, 4950–4959.
- (13) Dan, N. *Langmuir* **1996**, 4, 1101–1104.
- (14) Yerushalmi-Rozen, R.; Klein, J.; Fetters, L. J. *Science* **1994**, 263, 793–795.
- (15) Yerushalmi-Rozen, R.; Klein, J. *Langmuir* **1995**, 11, 2806–2814.
- (16) Yerushalmi-Rozen, R.; Klein, J. *Phys. World* **1995**, 8, 30–35.
- (17) Murat, M.; Grest, G. S. Computer Simulation of Tethered Chains. In *Monte Carlo and Molecular Dynamics Simulations in Polymer*; Binder, K., Ed.; Clarendon Press: Oxford, 1994.
- (18) Szleifer, I.; Carignano, M. A. *Adv. Chem. Phys.* **1996**, Vol. XCIV, 165–175.
- (19) Carignano, M. A.; Szleifer, I. *J. Chem. Phys.* **1993**, 98, 5006–5018.
- (20) Ben-Shaul, A.; Szleifer, I.; Gelbart, W. M. *J. Chem. Phys.* **1985**, 83, 3597–3611.
- (21) Szleifer, I.; Ben-Shaul, A.; Gelbart, W. M. *J. Chem. Phys.* **1986**, 85, 5345–5358.
- (22) Carignano, M. A.; Szleifer, I. *Macromolecules* **1995**, 28, 3197–3204.
- (23) Szleifer, I. *Biophys. J.* **1997**, 72, 595–612.
- (24) Szleifer, I. *Physica A* **1997**, 244, 370–388.
- (25) Carignano, M. A.; Szleifer, I. *J. Chem. Phys.* **1995**, 102, 8662–8669.
- (26) Carignano, M. A.; Szleifer, I. *Macromolecules* **1994**, 27, 702–710.
- (27) *Molecular Theory of Capillarity*; Rowlinson, J. S., Widom, B., Eds.; Clarendon Press: Oxford, 1982.

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