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Observation of autophobic dewetting on polymer brushes from computer simulation

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Abstract

We propose a method for direct calculation of an effective interface potential from computer simulation. The method allows us to locate the wetting transition, determine its order and calculate the concomitant contact angle of macroscopic drops. We illustrate the method by studying the wetting behaviour of a polymer melt on a brush consisting of chemically identical grafted polymers. At low grafting densities, the melt dewets; at intermediate grafting densities the liquid of free chains wets the brush. On further increasing the grafting density we encounter dewetting (autophobicity). When long-range forces are considered, autophobic behaviour is also observed, but the wetting transition is shifted to larger grafting densities and becomes first order.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The versatility of polymeric materials (monomer interactions, chain length, copolymerization, branching, etc) provides great control over the stability of thin polymer films. Many polymers, however, dewet smooth substrates, such as silicon wafers, and the resulting thin films prepared by spin coating often are unstable above the glass transition [1, 2]. An interesting issue is to understand and control such instabilities by surface modification. For example, the stability of polystyrene films on silicon substrates may be controlled by coating the surface with a layer of silicon oxide or a glassy polymer [3].

Alternatively, the wetting properties can be modified by grafting polymers onto the substrate via chemical reaction. The density of grafted chains becomes a control variable and it is expected that for large enough grafting densities, the enthalpic attraction provided by the grafted polymers on their free counterparts should result in a wetting transition. Unexpectedly, too high a grafting density results in *autophobicity*, the dewetting of a fluid on top of a film made of identical molecules [4–7]. This behaviour may be explained as a result of competing entropic factors: on the one hand, adsorption of the polymers within the brush provides an extra

translational entropy; on the other hand, this swelling comes at the expense of stretching the grafted polymers which, in turn, lose conformational entropy [8]. From this simple argument, it is predicted that a polymer will exhibit autophobic dewetting from a brush of chains of equal length for high enough grafting densities. Subsequently, these scaling considerations have been tested using self-consistent field (SCF) theory [9–12]. The entropic nature of the dewetting process has also been confirmed experimentally, as negative excess interfacial entropies were found for such systems in the autophobic regime [6]. Recently, an SCF theory was proposed [13] which incorporates an accurate equation of state for polymer melts [14] and thereby can deal with the substrate–brush, the brush–melt and the melt–vapour interfaces on the same footing. The theory was employed to study the wetting properties of short oligomers on a brush [15]. Our results confirmed the autophobic wetting behaviour and allowed us to study the interplay between short and long-range interactions by tuning the strength of the Hamaker constant [3] which leads to a complex wetting phase diagram.

In this paper we consider the autophobic dewetting of polymers on a brush by means of Monte Carlo simulations. A rather general methodology for the direct calculation of surface free energies [13, 16] is utilized and extended, so as to calculate effective interface potentials. This allows us to determine whether a substrate is wet or not and to obtain adsorption isotherms.

2. Molecular model and simulation methodology

Polymers are described by a coarse-grained bead-spring model [13, 14]. A bead interacts with every other bead of the system via a truncated and shifted Lennard-Jones potential:

$$V_{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 + \frac{127}{1024} \right] \quad \text{for } r \leq r_c \quad (1)$$

and $V_{\text{LJ}}(r) = 0$ otherwise. The cutoff distance is set to $r_c = 2 \times 2^{1/6}\sigma$. Polymer connectivity is realized by additional interactions between adjacent monomers within the same chain. These interactions take the form of a finitely extensible nonlinear elastic (FENE) potential, $V_{\text{FENE}}(r) = -kR_0^2 \ln(1 - \frac{r^2}{R_0^2})$ where the maximum allowed displacement between bonded monomers is $R_0 = 1.5\sigma$, while k , which plays the role of an elastic constant, is $k = 15\epsilon/\sigma^2$. Free and grafted chains comprise the same number of effective segments, $N = 10$. At the reduced temperature $k_{\text{B}}T/\epsilon = 1.68$, where k_{B} denotes Boltzmann's constant, the melt of monomer number density $\phi_l\sigma^3 = 0.611$ coexists with a vapour of density $\phi_v\sigma^3 = 0.0083$. The interface tension between the two coexisting phases is $\gamma_{\text{lv}}\sigma^2/k_{\text{B}}T = 0.0953$. The mean end-to-end distance of free chains in the melt takes the value $R_e = 3.66\sigma$ [13].

The substrate is modelled as an impenetrable, flat wall. The substrate properties are modified by grafting chain ends on the nodes of a square lattice with the first monomer of the grafted chain placed at a vertical distance of $z_{\text{g}} = 1.2\sigma$ away from the substrate. The properties of the brush that results are characterized by the surface area per grafted chain, Σ . The substrate interacts with the fluid via a potential of the form $V_{\text{wall}}(z) = A\{(\frac{\sigma}{z})^9 - (\frac{\sigma}{z})^3\}$, where A is the effective Hamaker constant characterizing all long-range interactions between the substrate and the polymer, while z is the perpendicular distance of a segment to the substrate. The simulation box of size $L_x \times L_y \times L_z$ has periodic boundary conditions in the x and y directions. The substrate is located at $z = 0$, while a purely impenetrable substrate is placed a distance L_z away.

We perform grand canonical Monte Carlo simulations where chain insertions/deletions are performed via the configurational bias technique. In addition, we utilize slithering-snake as well as local displacements. To obtain the effective interface potential we describe the configuration by the surface excess number of particles per area, $\Gamma = (Nn_{1/2} - \frac{1}{2}\phi_v V)/L_x L_y$,

where $n_{1/2}$ is the total number of molecules inside that half of the simulation box closest to the substrate, ϕ_v is the monomer vapour density at coexistence, and V denotes the total volume. While the surface adsorption is well defined, the distance, l , between the liquid–vapour interface and the substrate—the thickness of the polymer film—depends on both the adsorption and the shape of the density profile. Within the sharp interface approximation one obtains the simple relationship, $l \approx \frac{\Gamma}{\phi_l - \phi_v}$. The effective interface potential is then given by

$$g(\Gamma) \equiv -\frac{k_B T}{L_x L_y} \ln P_{1/2}(\Gamma) \quad (2)$$

where $P_{1/2}$ denotes the probability of observing a surface adsorption, Γ , inside the appropriate half box.

The relevant values of the adsorption range from the bare substrate to a thick liquid film. Sampling all such states in a single simulation run is difficult, because of the free energy barriers associated with the formation of a liquid film or liquid–vapour interface and the low relaxation times. Therefore we divide the whole range of interesting states between n_{\min} and n_{\max} into several smaller windows, of size $[n_i, n_{i+1}]$, and successively perform independent grand canonical simulations for each interval. The distributions of the individual runs are then patched together at their boundaries to obtain the full probability distribution up to an irrelevant normalization factor [17].

Note that once the interface potential at the coexistence chemical potential, μ_{coex} , has been determined, we can recover the resulting interface potential at any other chemical potential, μ , by Legendre transformation: $g_\mu(\Gamma) = g_{\mu_{\text{coex}}}(\Gamma) - \Gamma \Delta\mu$. This allows us to calculate adsorption isotherms, either in a mean field sense (minima of the interface potential), or accounting for fluctuations, since we can produce averages from $P(\Gamma) \sim \exp[-L_x L_y g(\Gamma)/k_B T]$. In this work we estimate the adsorption by performing an average over the distribution obtained from simulation.

3. Results

We first consider the proposed methodology for the calculation of effective interface potentials. We test the method for a substrate of low grafting density, $R_g^2/\Sigma = 1.23$, and zero Hamaker constant, $A = 0$, with a lateral system size $L_x = L_y = 13.2\sigma$ and box length $L_z = 90\sigma$. In order to study a broad range of adsorptions, we allow the system to explore states all the way between $n_{\min} = 0$ and $n_{\max} = 240$ free chains, and divide this segment into six smaller intervals of size $[0, 40]$, $[40, 80]$, \dots , $[200, 240]$. Figure 1(a) shows the six different probability distributions, $P_{1/2}$, that are obtained as we successively increase the number of windows employed to gather statistics. A probability distribution obtained by gathering statistics up to window i shows a spurious increase close to n_{i+1} , the maximum number of particles allowed in the simulation box for that window. However, the divergence may be shifted arbitrarily far away, by gathering information from an increasing number of windows. Matching the distributions at some arbitrarily chosen value of n (figure 1(b)), we find that all the distributions nicely collapse into a single curve. This master distribution is our estimate for the interface potential, $g(\Gamma)$.

We now consider the wetting behaviour of a series of substrates with increasing grafting density in the absence of long-range forces, i.e., $A = 0$. Figure 2(a) shows the effective interface potentials for grafting densities $R_g^2/\Sigma = 4.02, 6.03$ and 6.70 . For the lowest grafting density, we find a monotonic interface potential, with no apparent minimum at low adsorption. We conclude that for this grafting density, the melt wets the brush. Furthermore, the absence of structure in the interface potential is compatible with a second-order wetting transition, and

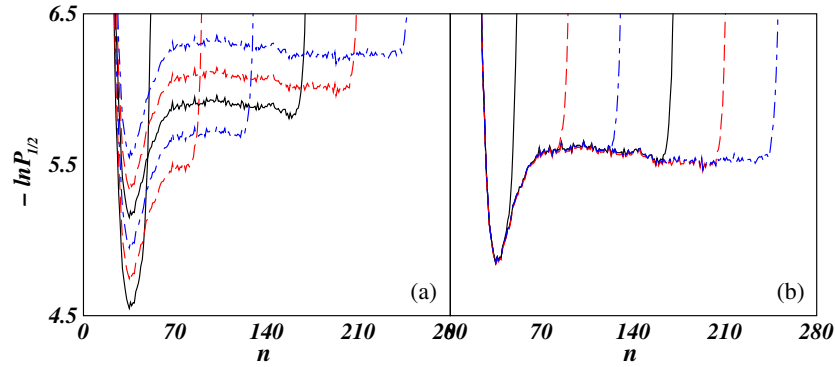


Figure 1. (a) Probability distribution of finding n chains a distance $L_z/2 = 12.3R_e$ or less away from the substrate. The figure shows the results obtained as an increasing number of windows are employed to gather statistics. The substrate consists of 16 grafted chains. Within the sharp interface approximation an adsorption of $n = 240$ chains corresponds to a film thickness of $l \approx 6.16R_e \ll L_z/2$. (b) Vertically shifted logarithmic distributions collapse into a single master distribution.

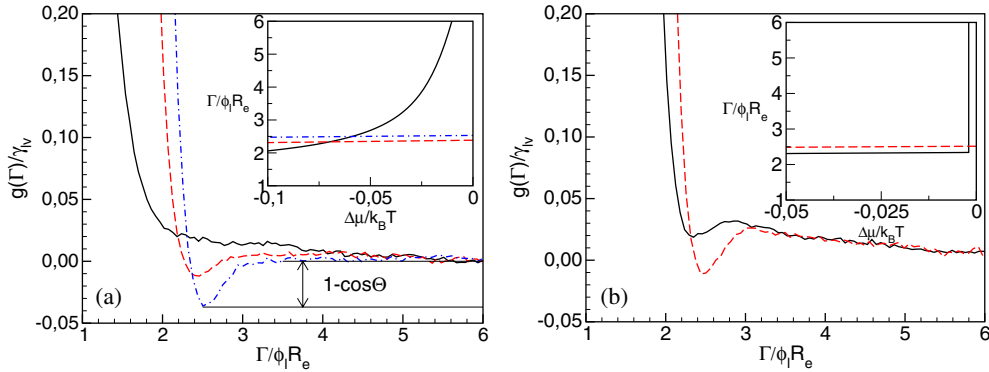


Figure 2. (a) Interface potentials as a function of total adsorption (graft + free) for three different grafting densities and $A = 0$. $R_e^2/\Sigma = 4.02$ (full line), 6.03 (dashed line) and 6.70 (dashed-dotted line). (b) As previously, for $A = 1.6$ and grafting densities $R_e^2/\Sigma = 6.03$ (full line) and 6.70 (dashed line). The inset shows the corresponding adsorption isotherms, with $\Delta\mu = \mu - \mu_{\text{coex}}$.

a corresponding complete wetting isotherm with no discontinuities. As the grafting density increases up to $R_e^2/\Sigma = 6.03$, however, the interface potential clearly exhibits an absolute minimum at low adsorption—the melt dewets from the brush. Increasing the grafting density to $R_e^2/\Sigma = 6.70$ increases the depth of the minimum.

The behaviour of the interface potential is corroborated by a study of the adsorption isotherms shown in the inset. For $R_e^2/\Sigma = 4.02$, the isotherm is seen to diverge as the chemical potential approaches coexistence, and further analysis (not shown) points to a nearly logarithmic divergence, as expected for short-range complete wetting [18]. For $R_e^2/\Sigma = 6.03$ and 6.70, however, the adsorption remains finite up to coexistence, indicating incomplete wetting. The extent to which the formation of a film is destabilized may be appreciated by considering the corresponding contact angles. These can be estimated from the interface potential: the depth of the minimum, Δg , is related to the contact angle, Θ , via

$\Delta g = \gamma_{lv}(1 - \cos \theta)$. Thus we estimate contact angles of macroscopic drops to be 10° and 16° for $R_c^2/\Sigma = 6.03$ and $R_c^2/\Sigma = 6.70$, respectively.

Adding long-range forces, we can make the melt wet the autophobic substrate. Balancing autophobicity against the attractive long-range forces gives rise to a first-order wetting transition [15]. Figure 2(b) shows interface potentials for grafting densities $R_c^2/\Sigma = 6.03$ and 6.70 and Hamaker constant $A = 1.6\epsilon$. For the lower grafting density, the absolute minimum of the free energy corresponds to a macroscopic adsorption, i.e., the attractive forces are strong enough to make the melt wet the dense brush. We clearly observe the presence of a metastable minimum at small adsorption which indicates that the wetting transition is first order. By keeping A constant but increasing the grafting density, autophobic dewetting results again, as can be seen from the interface potential at $R_c^2/\Sigma = 6.70$. This behaviour is confirmed by a study of the adsorption isotherms shown in the inset. For $R_c^2/\Sigma = 6.03$, a discontinuous jump in the isotherm is found very close to coexistence. Unfortunately, the system is so close to the wetting transition that finite equilibrium adsorption above the prewetting transition is larger than the largest adsorption sampled during the simulations. For $R_c^2/\Sigma = 6.70$, the adsorption remains finite and small up to coexistence, indicating incomplete wetting.

4. Conclusions

We have proposed a computational scheme which allows us to determine effective interface potentials. Although the method is computationally rather demanding due to the protracted long equilibration times of fluctuations of the film thickness, it is very powerful, for it allows us to determine the wetting properties of the substrate considered (contact angle, wetting transition, order of the transition, adsorption isotherms).

We have employed the technique in order to study autophobic dewetting. The results obtained indicate that there is a line of autophobic dewetting transitions in the space of A and $1/\Sigma$. These transitions are first order for $A > 0$ and second order for $A = 0$. The point where the autophobic first-order line meets the autophobic dewetting transition at $A = 0$ is expected to be a tricritical wetting point, in agreement with SCF calculations [15]. This complex behaviour results from the interplay between short-range entropic and long-range enthalpic interactions.

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