

First-order wetting transition at finite contact angle

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(Received 2 May 2002; revised manuscript received 12 August 2002; published 11 November 2002)

The wetting of a polymer brush by a melt of similar chains can have a window of complete wetting with a classical allophobic wetting transition at low grafting density σ and an autophobic one at high σ . However, when the melt chains are much longer than the brush chains, the contact angle α goes through a nonzero minimum where $\partial\alpha/\partial\sigma$ has a jump. A self-consistent-field analysis and experimental observations indicate a double-well disjoining pressure curve, consistent with a first-order wetting transition at finite α . The metastable contact angle can become zero.

DOI: 10.1103/PhysRevE.66.051801

PACS number(s): 61.25.Hq, 68.08.Bc, 61.30.Hn

The control of the wettability of surfaces is an important aspect in many research fields spanning the full spectrum from fundamental science to engineering. One way to tune the wettability is to modify the surface by grafting molecules onto them. End grafting of macromolecules onto surfaces is an interesting option. When the chains are “planted” such that they strongly laterally interact, one obtains a so-called (polymer) brush. Results of a wetting study of how end-grafted polymer molecules (brush) influence the wetting of a solid substrate by a melt of similar chains is reported in this paper. Our theoretical and experimental results show that the current wetting theory does not cover all possible scenarios.

Classical wetting theory [1,2] allows strictly for first- and second-order wetting transitions from partial, the contact angle $\alpha > 0$, to complete wetting, where $\alpha = 0$. For a continuous wetting transition (second order), the contact angle goes smoothly to zero. However, a first-order wetting transition features a contact angle that is nondifferentiable at the transition. Wetting transitions at finite contact angle are not envisioned by the classical wetting theory and have never been reported in the literature.

Wetting problems are complex because one always should consider three phases. Typically, but not necessarily, one of the phases is a solid substrate. The other two phases may be a binary liquid with a solubility gap, or a liquid with its vapor. Usually, the wetting theory is discussed in the setting of a solid substrate in contact with a liquid-vapor system. In the present paper we discuss a solid substrate (with on top a polymer brush) in contact with a polymer melt-vapor system.

It is essential to mention that wetting transitions occur *at bulk coexistence*, that is, the condition (chemical potential of the liquid molecules) that exists when a macroscopic amount of liquid is in equilibrium with its vapor. These should be distinguished from (first-order) prewetting transitions. At a prewetting transition, there is a small jump in film thickness from a microscopic to a mesoscopic value, which occurs off-coexistence. The prewetting steps become more pronounced when they occur closer to the coexistence value and merge with the (first-order) wetting transition where the step in the isotherm diverges. It is interesting to note that the number of interfaces in the system is higher when the contact angle is finite than when the contact angle is zero. It has been argued that wetting transitions are true transitions just because of this reduction of the number of interfaces that can exist at coexistence [2].

The wetting behavior near a solid substrate onto which a polymer brush is administered is unusual, basically because there are interactions on two length scales that influence and determine the overall wetting behavior [3,4]. First of all there is the solid substrate. Interactions of the polymer chains with this substrate are of short-range nature (the effect of long-range van der Waals interactions will be mentioned below). If the system is partially wet, the surface is allophobic with respect to the melt. Second, there is the polymer brush. Typically, the grafted chains may assist in obtaining a low contact angle and in favorable cases the surface may be wetted ($\alpha = 0$). When the melt does not wet its own brush (this occurs as we will see, e.g., when the grafting density is too high), this is known as autophobicity. The structure of the polymer brush as a function of the grafting density σ is well known. When the end-grafted chains laterally overlap, the chains must stretch strongly outwards and the brush height becomes a linear function of the length N of the chains, i.e., $H \propto N$ [5–10]. In this limit the wetting behavior is determined by the nature of the brush and the interactions occur on the length scale proportional to (up to) H . At intermediate grafting densities, $\sigma N \approx 1$, one may expect an interplay between interactions from the substrate and those originating from the brush.

According to the above, when the polymer melt does not wet the surface (i.e., the allophobic regime) one may graft chains onto the surface to improve the wettability. These grafted chains are typically collapsed as a globule onto the surface when the substrate is in contact with the air (vapor). When the melt is applied on top of the substrate, the grafted chains can assume Gaussian-like conformations and this swelling is the driving force for the wetting transition. In order to have such swelling of the grafted chains, they should be accepted by the melt. Thus, there may be no enthalpic effects while mixing the grafted chains with the melt chains. Therefore, the grafted chains should preferably be chemically identical to the melt chains. Upon increasing the grafting density of the polymer chains on the surface, it is known that the properties of the brush become essentially independent on the substrate onto which they are grafted. This is the reason why the wetting of a brush by chemically identical melt chains, as reported in the literature, rarely takes the properties of the surface into account. According to the literature one should expect an autophobic wetting transition,

e.g., at high grafting density. The physical origin of this wetting transition is basically understood [11,12]. At high grafting density, the chains in the brush are strongly stretched. The segment density of anisotropically stretched chains in the brush may even exceed the segment density of the (weakly compressible) melt. The chains in the polymer melt that are placed on top of the brush are in random coil conformations. These chains can gain no free energy (in this case they cannot gain entropy) by penetrating into the highly oriented (and a bit denser) brush. Therefore at sufficiently high grafting density an autophobic wetting transition is expected and seen experimentally [13–16]. Also in the limit of grafting density unity, that is, when all the chains in the brush are in the extended upright conformation, the top of the brush is an impenetrable substrate again. The polymer melt chains experience conformational entropy loss near such a surface and this entropy loss is the reason why the polymer melt does not wet the solid substrate made of chemically identical molecules [17]. The two wetting transitions (allophobic and autophobic) discussed above depend obviously on the properties of the solid substrate and, when the chemical identity of the brush and the melt chains is insisted upon, on the chain length disparity between the brush chains and the melt chains. Below we will fix the surface properties and elaborate on the effect of the chain length difference between the melt and the brush chains.

Our theoretical approach is based upon a numerical self-consistent-field analysis, making use of the discretization scheme of Scheutjens and Fleer (SF-SCF). This theory has been applied to the wetting of polymer brushes before [3,18]. The method allows for the evaluation of the equilibrium density profiles of the relevant interfaces in the system as well as an accurate evaluation of the (mean field) surface free energies. In the method, only short-range nearest-neighbor contact energies are accounted for and parametrized by the well-known Flory-Huggins interaction parameters. The model system is designed such that there are minimum number of parameters. To this end we introduce a substrate composed of units of type S with a fixed Fresnel-like structure: the volume fraction $\varphi_S(z)=1$ when $z \leq 0$ and zero otherwise (z is thus the spatial coordinate which gives the distance to the wall; all linear dimensions are normalized to the segment size). Onto this interface flexible chains with length N composed of units of the type S , $(S)_N$ are end grafted, i.e., the first segment is restricted to $z=1$. The wetting component is a melt composed of homopolymers of length P composed again of segments of type S , i.e., $(S)_P$. The compressibility of the melt plus brush system is realized by introducing a monomeric solvent $(V)_1$, which may be interpreted as vacancies. In this case the SF-SCF method is similar in spirit to a classical lattice-gas theory. The only Flory-Huggins interaction parameter is the one between V and S , i.e., χ_{VS} . The value used for this parameter is chosen such that the polymer-vapor system has a pronounced solubility gap, i.e., there is a sharp polymer-vapor interface. Throughout this work a value of $\chi_{VS}=1$ is used. The grafting density, i.e., the number of grafted chains per unit area, σ is varied but the length of the grafted chains is fixed to $N=200$. The statisti-

cal weights of chain conformations are generated by a propagator formalism that is the discrete version of the Edward-diffusion equation [19]:

$$\frac{\partial G(z;s)}{\partial s} = \left(\lambda \frac{\partial^2}{\partial z^2} - u(z) \right) G(z;s), \quad (1)$$

where s is the parameter counting the distance along the contour of the chain. This equation is complemented with the appropriate boundary (absorbing near the surface and reflecting at a distance far from the surface) and initial conditions (i.e., grafting condition for the brush chains). The SF-SCF formalism features a segment potential $u(z) = \ln[\varphi_V^b/\varphi_V(z)] + 2\chi_{SV}(\langle \varphi_V(z) \rangle - \varphi_V^b)$. The angular brackets account for non-local interactions $\langle \varphi_V(z) \rangle \approx \varphi_V(z) + \lambda \partial^2 \varphi_V(z)/\partial z^2$ and $\varphi_V^b \approx 1$. These nonlocal contributions are essential for the correct analysis of interfacial problems. The segment densities follow from two complementary Green's functions, one computed with Eq. (1) starting from segment $s=1$ leading to $G(z;s)$ and, the other one starting from the other end $s=N$ (or P) leading to $G^{inv}(z;s)$: $\varphi(z) = C e^{u(z)} \sum_s G(z;s) G^{inv}(z;s)$. The normalization for the grafted chains is proportional to the grafting density whereas the normalization for the melt chains is fixed by the amount Θ of melt in the system.

For a particular self-consistent-field solution (which is obtained numerically), the segment potentials and the segment densities are internally and mutually consistent. On top of this, the local volume fractions add up to unity, i.e., $\varphi_V(z) = 1 - \varphi_S(z)$ for all coordinates z . For such a SCF solution the relevant structure of the interfacial layer may be analyzed. Important for the study of wetting transitions is the accurate evaluation of the interfacial free energies. Let us refer to the vapor as V , the solid as W , and the melt as L . Then three interfacial tensions may be defined: γ_{WV} , γ_{WL} , and γ_{LV} for the wall-vapor, the wall-liquid, and the liquid-vapor tensions, respectively. The contact angle is easily obtained from Young's law:

$$\begin{aligned} \cos \alpha &= \frac{\gamma_{WV} - \gamma_{WL}}{\gamma_{LV}} = 1 + \frac{\gamma_{WV} - (\gamma_{WL} + \gamma_{LV})}{\gamma_{LV}} \\ &= 1 + \frac{\gamma_{thin} - \gamma_{thick}}{\gamma_{LV}}, \end{aligned} \quad (2)$$

which defines both γ_{thin} and γ_{thick} as two interfacial tensions that are readily available from the calculations. The remaining surface tension γ_{LV} is found from the equilibrium vapor-melt interface. In our calculations $\gamma_{LV}=0.13483$ in units of $k_B T$ per site.

In Fig. 1(a) the contact angle is plotted as a function of the grafting density σ for $P=100,500$. When $P < N$, there is a window of complete wetting, i.e., the contact angle (for $P=100$) is zero in the range $0.0052 < \sigma < 0.122$. It is evident that the wetting transition at low grafting densities is of first order. The $\alpha(\sigma)$ pinches upon the $\alpha=0$ axis with a finite angle. The wetting transition at high grafting densities is of second order. This is in line with recent work of Mueller and

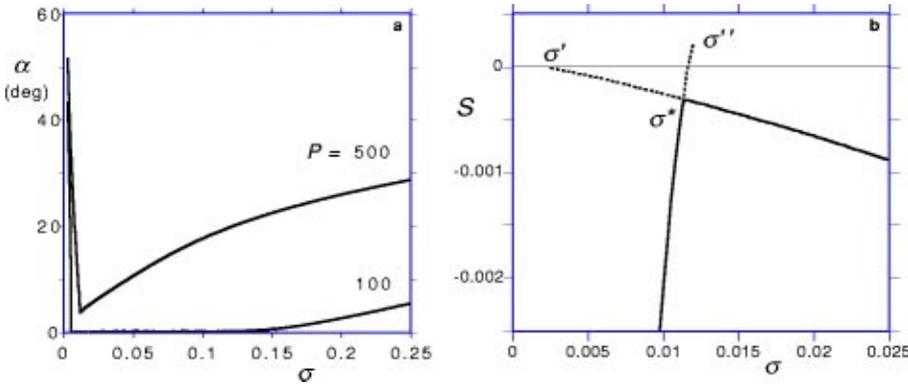


FIG. 1. (a) The contact angle of the melt with chains of length P as indicated as a function of the grafting density of the chains in the brush. (b) The spreading parameter $S = \gamma_{thin} - \gamma_{thick}$ as a function of the grafting densities for $P = 500$, the binodal point σ^* as well as metastable (dotted) parts up to the points σ' and σ'' are indicated.

Dowell [15]. With a similar SCF technique they also report first- and second-order wetting transitions.

For the following analysis it is not necessary that this last transition is indeed of second order. Long-range van der Waals forces may cause this transition to be of first order as well without consequences for our arguments. When $P > N$, the contact angle does not reach the wetting value $\alpha = 0$ and remains finite for all values of the grafting density σ . Interestingly, the curve of $\alpha(\sigma)$ is not a smooth function; there is a sharp break at $\sigma^* = 0.0113165$.

A few relevant adsorption isotherms, in which the excess amount $\Gamma \approx \Theta$ of polymer melt chains is given as a function of the chemical potential, are plotted in Fig. 2(a). Here we have collected results for a grafting density just below, close to, and just above σ^* . The isotherms have a pair of van der Waals-like loops. The one at lowest Γ is a residual feature of the first-order wetting transition as found for systems with small values of P . The second loop at higher Γ is the residual of the second-order wetting transition for smaller P . It is necessary to understand which parts of the loops are stable and which parts are metastable or unstable. This may be investigated using the classical Maxwell constructions. An alternative is to investigate the cusplike figures found by plotting the surface free energy as a function of the chemical potential. In Fig. 2(b) the three cusplike figures are shown. When two lines (for a given σ) in such a figure cross (in

such a way that with increasing film thickness the chemical potential increases and the surface free energy decreases), a phase transition is found. The lower branch of the surface free energy is always the most favorable one and represents the stable branch.

The inspection of Fig. 2(b) shows that for $\sigma > \sigma^*$ there are lines crossing at a value of the chemical potential which is below the saturation value. This means that there is a jump (first-order transition) from a microscopic to a mesoscopic film thickness that occurs off-coexistence. Again this is a prewetting transition, and is similar to the classical case associated with the first-order wetting transition at σ^* . We discussed before [3] the unusual scenario of having a prewetting step in the isotherm in connection with partial wetting, however, this phenomenon has not yet been associated with the wetting transition discussed in this paper. In Fig. 2(b) the lines in the cusp cross exactly at the coexistence value for $\sigma^* = 0.0113165$. This is the special condition which signals a true wetting transition in the system; the jump occurs at coexistence. In Fig. 2(b), the cusped figure has no crossings of lines for $\sigma = 0.011 < \sigma^*$ and thus at this grafting density there is no jump in adsorbed amount. There exist, however, values for σ such that $\sigma^* > \sigma > 0.011$ for which the step in the isotherm occurs at $\mu > \mu^\#$. These transitions may be called postwetting transitions. We haste to mention that postwetting transitions cannot be observed experimentally because they occur for $\mu > \mu^\#$.

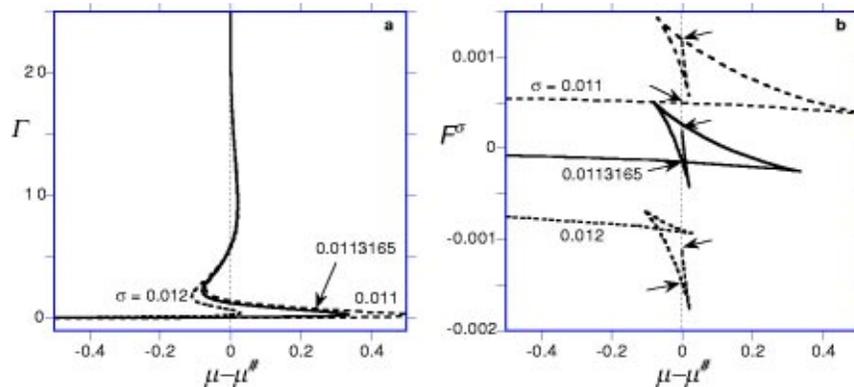


FIG. 2. (a) Adsorption isotherms of the excess amount of polymer melt chains $P = 500$ on the surface as a function of the normalized chemical potential for three values of the grafting density of the brush. The chemical potential at coexistence is given by $\mu^\#$. (b) The corresponding surface free energy (shifted and in units of $k_B T$ per site) versus normalized chemical potential (in units of $k_B T$). The vertical dotted line represents the coexistence values. The arrow pointing to the right gives the value of $F^\sigma = \gamma_{thin}$, the arrow pointing to the left gives $F^\sigma = \gamma_{thick}$.

The curve of $F^\sigma(\Gamma)$ ends at $\mu^\#$, indicated by the vertical dotted line. If this end point is the lowest in F^σ , the system is wet. If it is not the lowest point at coexistence, the system is partially wet. From the cusps in Fig. 2(b) it is concluded that all three cases correspond to partial wetting: the surface free energy at coexistence for the thick film (indicated by the arrows pointing to the left) is higher than the corresponding surface free energies of the thin films (arrows pointing to the right). The contact angle is proportional to this difference [see Fig. 1 and Eq. (2)].

Results of Fig. 2 thus prove the first-order character of the transition at σ^* . Below the transition, $\sigma < \sigma^*$, the contact angle is found by comparison of the surface free energies of the microscopically thin and the macroscopically thick films. Above the transition, i.e., when $\sigma > \sigma^*$ the contact angle is found from comparison of the surface free energies of the mesoscopically thick film in relation to the macroscopic film. Exactly at the transition, the jump in the adsorbed amount from microscopic to mesoscopic amounts of the wetting component occurs at the coexistence value. In other words, a macroscopic drop will coexist at the wetting transition with two film thicknesses. One of these films is microscopically thin and the other is of mesoscopic size. Associated with this first-order transition there are classical prewetting and non-classical (experimentally inaccessible) postwetting transitions. Of course the prewetting step does not diverge when it merges with the wetting transition at coexistence because the contact angle at the transition is not zero.

The binodal for the first-order transition is located at the transition σ^* . Spinodal points may also be identified as the end points of metastable lines. Using this ansatz, the two spinodal points are referred to as σ' and σ'' and are indicated in Fig. 1(b). In this figure the spreading parameter S is plotted as a function of the grafting density. The system is partially wet when $S < 0$ and completely wet when $S \geq 0$. The metastable branches of $S(\sigma)$ curves are dotted in Fig. 1(b). The metastable branches were found by computing the contact angle using the surface free energy difference between the (metastable) microscopic thick film and the macroscopic thick film in the case that $\sigma > \sigma^*$, and the surface free energy difference between the (metastable) mesoscopic thick film and the macroscopic thick film in the case that $\sigma < \sigma^*$. Interestingly it is found that in the metastable branches the spreading parameter S can assume the complete wetting value $S = 0$. This means that the metastable contact angle can go to zero. It is expected that the lifetime of the metastable wetting layers (with $\alpha = 0$) is very long. This observation is of importance for the understanding of dewetting kinetics of polymer films on brushes [20,21]. It is of interest to mention that the “spinodal point” σ' occurs exactly at the value $S = 0$, whereas the other point σ'' occurs (in this case) for $S > 0$. The possibility to have metastable films vanishes smoothly at σ' and the end point σ' behaves as a second-order transition. Interestingly, the possibility to have metastable states vanishes at σ'' in a jumplike fashion.

If the adsorption isotherm is rotated by 90° , and when the adsorbed amount Γ is translated into a film thickness d (there is a trivial one-to-one relation), one obtains a so-called disjoining pressure Π vs d diagram. Fig. 2(a) thus proves that

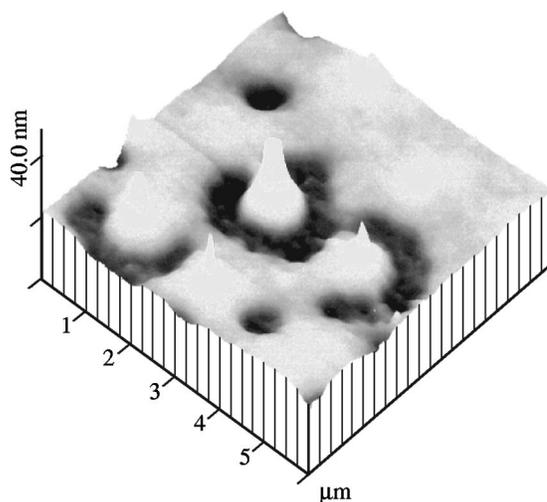


FIG. 3. An atomic force microscopic (AFM) image of a $6 \times 6 \mu\text{m}$ area of the dewetting patterns found when a melt of polystyrene (PS) with length $P \approx 1800$ was annealed on a brush of the same molecules. Bright spots are the highest point, the black regions are the regions with a very thin polymer film. Experiment: a silica surface was covered by a poly-4-vinylpyridine (PVP) layer. The PS chains (end grafted on the PVP) had a length $N \approx 200$ and a density of $\sigma \approx 0.2$ chains per nm^2 . The melt was spin coated on the brush and annealed under *vacuo* at $T = 145^\circ\text{C}$ for 12 days. More details on the experimental conditions are found in Ref. [18].

$\Pi(d)$ features a double minimum especially in the region where the contact angles are small. Such a disjoining pressure curve was already anticipated by Landau and Lifshitz [22]. We have experimental evidence that such a double-minimum disjoining pressure curve exists in an experimental system. In Fig. 3 we present an atomic force microscopic image showing a dewetting pattern of a thin polystyrene (PS) film spin coated on a PS brush. The dewetting occurs for $P > N$ and at intermediate grafting densities, by the breakup of the homogeneous film such that “hills” (small drops) form surrounded by “holes” immersed in regions with intermediate film thickness. Throughout the mesoscopically thin film there are also isolated spherical holes and isolated hills (drops). Apparently, the drop can coexist with two film thicknesses, one microscopically thin and another mesoscopically thin. Such peculiar dewetting patterns are consistent with the SCF calculations and with a double-well character of the disjoining pressure. Direct simulations of the dewetting patterns of thin polymer films have recently been performed by Sharma and Khanna [23]. They applied Navier-Stokes fluid dynamics to thin films. The finite film-size effects were included by an arbitrary shape of the disjoining pressure curves. Application of this method to a double-well disjoining pressure diagram resulted in patterns very similar to these shown in Fig. 3. The characteristic hills and holes pattern in an otherwise homogeneous film with intermediate thickness does not appear when the disjoining curves are classical, i.e. when there is just a single minimum.

The wetting transition at finite α conserves the number of interfaces and thus the argument mentioned above that this number should change at a wetting transition is invalid. Moreover, the fact that one can have wetting transitions at a

finite contact angle damages the framework of the classical wetting theory. The classical wetting theory exclusively deals with *complete* wetting transitions, where the adjective “complete” refers to the wetting condition at $\alpha=0$. The classical wetting theory suffices when the wetting component has interactions with the substrate essentially on one length scale. Then only complete wetting transitions can occur. If the interactions of the wetting component with the substrate are more complex, that is, when interactions on two (or more) distinct length scales are present, the wetting behavior is more rich than anticipated by the classical wetting theory. As a consequence, the classical wetting theory must be extended to account for *incomplete* wetting transitions. The adjective “incomplete” points to the wetting transitions at finite contact angle $\alpha>0$. Such an extension is not a minor one. When first-order phase transitions are considered, one typically can distinguish binodal (that is, the exact transition point) and spinodal conditions, where the system becomes intrinsically unstable. Between the binodal and spinodal conditions, the system is metastable. Complete wetting transitions occur at $\alpha=0$. As it is impossible to have $\alpha<0$, it does not make sense to discuss metastable branches or spinodal conditions in the context of complete wetting transitions. However, this is no longer the case when a first-order wetting transition occurs at a finite $\alpha=\alpha^*>0$ (incomplete wetting transitions).

In this case the region $0<\alpha<\alpha^*$ is accessible. As was shown above, one can find meaningful metastable states and spinodal conditions. This finding is of large importance to understand the kinetics of dewetting. Indeed, the incomplete wetting transition (at finite contact angle) is in line with the phase transition theory [22] and should be considered more classical than the complete wetting transitions at $\alpha=0$.

Of course there exists a rather conservative solution to save the classical wetting theory. One may decide that the wetting transition is just one member of the family of surface phase transitions. Wetting transitions are those surface phase transitions that deal with the change from partial to complete wetting, that is, at $\alpha=0$. In this restricted view it is not necessary to identify the difference between complete wetting or incomplete wetting transitions as introduced above. The first-order transition discussed in this paper is then just another surface phase transition, to be distinguished from a wetting transition. The disadvantage of choosing for this way out is that it is not obvious how then one shall differentiate between, e.g., surface phase transitions that occur *on-* or *off-*coexistence. Indeed, it will prove necessary to introduce the same terminology as in wetting theory for the more general surface phase transitions. This type of redundancy in languages appears not very elegant to us.

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