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Wetting of a short chain liquid on a brush: First-order and critical wetting transitions

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Abstract. – We investigate the wetting behaviour of short chains on a surface covered with a brush of end-grafted chains of the same architecture by a combination of self-consistent field calculations and liquid-state theory. The surface interacts with the monomers via (non-retarded) van der Waals interactions of strength A . At low grafting densities, we find first-order wetting transitions. The value of the effective Hamaker constant $A_{\text{wet}} > 0$, at which the transition occurs, decreases and the strength of the first-order transition becomes weaker as we increase the grafting density. In an intermediate range of grafting densities, we encounter second-order wetting transitions at a vanishing Hamaker constant $A_{\text{wet}} = 0$. The second-order transition is preceded by a first-order transition between a thin and a thick liquid layer (“frustrated” complete wet state) at negative values of A . This line of first-order transition terminates in a critical point. Upon increasing the grafting density further, we encounter a tricritical point, beyond which the wetting transition is again of first order and occurs at $A_{\text{wet}} > 0$. At these high grafting densities, the brush expels the free chains (autophobicity).

Introduction. – Grafting or adsorbing polymer chains on surfaces has been employed successfully to tailor surface properties [1–4]. If a liquid does not wet a solid substrate, homogeneous thin liquid films are unstable and break up to form droplets. Grafting polymers onto the surface may “tie down” [2] the liquid film and prevent rupture. This property is desirable in practical applications ranging from dielectric coatings, adhesion, and lubrication to biocompatibility.

We consider the wetting of an oligomeric liquid on top of a chemically identical brush. According to the Young equation [5], the polymer liquid will wet the brush if $\gamma_{\text{BL}} + \gamma_{\text{LV}} \leq \gamma_{\text{BV}}$, where γ_{BL} , γ_{LV} , and γ_{BV} denote the tension of the brush-liquid, liquid-vapour, and brush-vapour interfaces, respectively. Typically, the tension at the liquid-vapour and brush-vapour interface are large and of comparable magnitude, while the free-energy cost of the interface between brush and the free chain liquid is small.

Scaling considerations [6, 7] and self-consistent field calculations [8–11] of incompressible melts with purely repulsive interactions have been applied with success to the manner in which a concentrated solution of free chains penetrates into the brush. At low grafting densities the penetration is large and γ_{BL} is negative, but there is little penetration at large grafting densities and γ_{BL} is positive. This dependence on the grafting density partially rationalises the experimental observation that a polymer liquid does not wet a brush of identical monomers at high grafting densities [3, 12, 13]. The properties of the liquid-vapour or brush-vapour interface,

however, cannot be described by models which invoke an incompressibility constraint and the effect of long-ranged van der Waals interactions between the liquid and the substrate is often neglected [8].

In this note we obtain the wetting properties of an oligomeric liquid on a brush made of identical chains by a recently developed combination of self-consistent field and liquid-state techniques [14]. This allows us, for the first time, to investigate the liquid-vapour and the liquid-brush interface within a unified framework. We investigate the interplay of the grafting density and the strength of the van der Waals interactions between monomers and substrate. The wetting phase diagram is surprisingly rich and comprises first-order and critical wetting transitions, a “frustrated” complete wet state, a critical end point and a tricritical wetting transition.

Model and technique. – The wetting phase diagram is calculated by self-consistent field calculations in the framework of a bead spring model of $N = 10$ units. Each pair of beads interacts via a shifted Lennard-Jones potential $V_{\text{LJ}}(\mathbf{r}) = 4\epsilon\{(\sigma/r)^{12} - (\sigma/r)^6\} + 127\epsilon/4096$ which is cut off at $r_{\text{max}} = 2 \times 2^{1/6}\sigma$. Monomers along a chain are bonded via a FENE potential $V_{\text{FENE}}(\mathbf{r}) = -15\epsilon(R_0/\sigma)^2 \ln(1 - r^2/R_0^2)$, with $R_0 = 1.5\sigma$. These parameters are commonly used in computer simulations [15]. In the following all energies are measured in units of the Lennard-Jones parameter ϵ . The substrate is modelled as impenetrable and ideally flat. Monomers at a distance z away from the substrate experience a van der Waals potential: $V_{\text{wall}}(z) = |A|(\sigma/z)^9 - A(\sigma/z)^3$ [16]. Since the monomer-monomer interactions are of finite range, $V_{\text{wall}}(z)$ is the only long-ranged interaction and A is proportional to the effective Hamaker constant. We calculate the wetting behaviour at temperature $T = 1.68$, where the polymer vapour has a negligible concentration ($\langle\phi\rangle_v = 0.0015$) and the monomer number density of the liquid is $\langle\phi\rangle_l = 0.634$ [17]. At this temperature/density we expect our model to exhibit the generic behaviour of a polymer solution well below the Θ temperature. The behaviour in the vicinity of the Θ temperature may differ from our results as the width of the liquid-vapour interface exceeds the coil extension.

The thermodynamics of the homogeneous system is obtained via Wertheim’s thermodynamic perturbation theory (TPT1) [18]. We calculate the properties of the reference system of non-bonded monomers via the Ornstein-Zernike equation using the reference hypernetted chain closure. The TPT1 treats the bonding potential as a perturbation. It yields good agreement with Monte Carlo simulations for the phase behaviour [17].

In the inhomogeneous system we make a weighted density functional ansatz for the monomer-monomer interaction F_0 in terms of the monomer number density $\phi(\mathbf{r})$ [14,19]:

$$\frac{F_0[\phi]}{k_{\text{B}}T} = \int d^3\mathbf{r} \phi(\mathbf{r}) f(\bar{\phi}(\mathbf{r})), \quad \text{with} \quad \bar{\phi}(\mathbf{r}) = \int d^3\mathbf{r}' w(\mathbf{r} - \mathbf{r}') \phi(\mathbf{r}'). \quad (1)$$

The free-energy density f is completely determined by the thermodynamics of the homogeneous system. The weight function w is normalised to unity and for our calculations we employ the choice: $w(\mathbf{r}) \sim -10(\sigma - |\mathbf{r}|)$ for $|\mathbf{r}| < \sigma$ and $w(\mathbf{r}) \sim -V_{\text{LJ}}(\mathbf{r})/k_{\text{B}}T$ for $|\mathbf{r}| > \sigma$. The weighting function introduces fluid-like packing effects and partially incorporates the effect of missing attractive interactions at the surface. The specific form yields a reasonable description of the packing at an attractive wall as observed by Monte Carlo simulations [14]; however, we do not expect the qualitative features of our calculations to depend on the details of w .

We consider the partition function in the grand-canonical ensemble [9]

$$\mathcal{Z} \sim \sum_{n_{\text{f}}} \frac{\exp[\mu n_{\text{f}}/k_{\text{B}}T]}{n_{\text{f}}!} \int \mathcal{DP} \exp \left[-\frac{F_0}{k_{\text{B}}T} \right], \quad (2)$$

where μ denotes the chemical potential of the free chains and the sum runs over all possible numbers n_f of free chains. \mathcal{D} sums over all conformations of all (both grafted and free) polymers, while \mathcal{P} denotes the probability distribution of a gas of (mutually non-interacting) chains including the interaction with the wall. The partition function cannot be evaluated explicitly, and we employ mean-field theory, which approximates the interacting many-chain problem by that of a single chain in a self-consistently determined external field u . Let

$$\mathcal{Q}_g = \int \mathcal{D}\mathcal{P}_{g1}[\{r_i\}] \exp \left[- \sum_{i=1}^N \frac{u(r_i)}{k_B T} \right] \quad \text{and} \quad \mathcal{Q}_f = \frac{1}{L^2 D} \int \mathcal{D}\mathcal{P}_{f1}[\{r_i\}] \exp \left[- \sum_{i=1}^N \frac{u(r_i)}{k_B T} \right] \quad (3)$$

denote the single-chain partition functions of a grafted and a free chain in the external field u , respectively. L and D are the system dimensions parallel and perpendicular to the substrate. For the calculations we employ $D = 16\sigma$. We evaluate the single-chain partition function via a partial enumeration over 10^6 – 10^7 conformations of free and grafted chains and achieve an accuracy of $\mathcal{O}(10^{-4})$ in the free-energy density. Conformations are generated by Monte Carlo simulations at $T = 1.68$ and liquid density. The first monomer of a grafted chain is located a distance $z_0 = 1.2\sigma$ away from the substrate, while the free chains sample all possible locations.

The grand-canonical free-energy density in units of $k_B T$ takes the form

$$g \equiv -\frac{\ln \mathcal{Z}}{L^2 D} = -e^{\mu/k_B T} \mathcal{Q}_f - \frac{1}{\Sigma D} \ln \mathcal{Q}_g + \frac{1}{L^2 D} \int d^3 \mathbf{r} \left(\phi f(\bar{\phi}) - u \phi \right), \quad (4)$$

Σ denotes the average area per grafted chain. The field u and the monomer density of free ϕ_f and grafted chains ϕ_g satisfy the set of self-consistent equations

$$\frac{u(\mathbf{r})}{k_B T} = \frac{\mathcal{D}}{\mathcal{D}\phi(\mathbf{r})} \frac{F_0[\phi]}{k_B T} = f(\bar{\phi}) + \int d^3 \mathbf{r}' w(\mathbf{r} - \mathbf{r}') \phi(\mathbf{r}') \frac{df}{d\bar{\phi}}, \quad (5)$$

$$\phi_f(\mathbf{r}) = -V e^{\mu/k_B T} \frac{\mathcal{D}\mathcal{Q}_f}{\mathcal{D}u(\mathbf{r})} \quad \text{and} \quad \phi_g(\mathbf{r}) = -\frac{L^2}{\Sigma \mathcal{Q}_g} \frac{\mathcal{D}\mathcal{Q}_g}{\mathcal{D}u(\mathbf{r})}; \quad \phi(\mathbf{r}) = \phi_f(\mathbf{r}) + \phi_g(\mathbf{r}). \quad (6)$$

The local densities are proportional to the Boltzmann average of the density created by a single chain in the external field u . The local external field, in turn, depends on the density. Spatial dependencies are discretised in terms of the real space coordinate z perpendicular to the surface with a typical resolution of $\Delta z = 0.16\sigma$. We solve the corresponding set of non-linear equations via a modified Newton-Broydon scheme.

Results. – In fig. 1 we present the grand-canonical free energy per unit area as a function of the thickness of the polymer layer $l \equiv \int dz \phi(z)/\langle \phi \rangle_1$ in the absence of long-ranged interactions. At very low grafting densities the free energy exhibits a minimum at a microscopic thickness of the liquid film. This thickness depends only very weakly on the grafting density. As we increase the thickness l of the layer further, the free energy rises, passes through a maximum, and becomes independent of the thickness for very large values. We chose this limiting value as reference. Upon increasing the number of grafted chains the free energy at the minimum increases and at $R_e^2/\Sigma = 0.507$ we find a first-order wetting transition, where the free energy of a stable thin film equals the free energy of a macroscopically thick film.

At intermediate values of the grafting density, the liquid wets the brush in the absence of long-ranged forces, and g decreases monotonically: The dry brush collapses in a bad solvent. Penetrating the brush, the free chains gain translational entropy and the grafted chains gain conformational entropy as they can swell to their unperturbed dimension R_e (cf. fig. 2(a)).

With increasing the grafting density further, however, the grafted chains stretch and a minimum appears again in the free energy as a function of the film thickness l : The interface of a

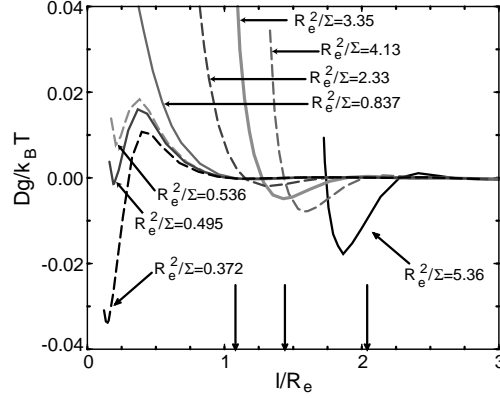


Fig. 1 – Grand-canonical free energy per unit area as a function of the film thickness l for various grafting densities R_e^2/Σ as indicated in the key. There are no long-ranged interactions ($A = 0$) between the substrate and the monomers. (The arrows on the abscissa correspond to the film thickness in fig. 2 and $R_e^2/\Sigma = 3.35$ (thick line).) The average end-to-end distance is $R_e = 3.66$.

dry brush in contact with the vapour is as narrow as the liquid-vapour interface (cf. fig. 2(b)). Addition of a small amount of free chains to a dry brush reduces the free energy, because it allows the brush to adopt a wider density profile. The free chains concentrate at the top of the brush and form a narrow liquid-vapour interface. Adding more free chains than required for relaxing the density profile of the brush increases the free energy. The density profile of the brush remains unaltered and free chains are rather confined to a thin liquid layer on top of the brush. Their configurations are restricted and the concomitant depletion interaction between the brush-liquid and the liquid-vapour interface creates an attraction between the brush-liquid and the liquid-vapour interface [10]. Hence, the liquid does not wet the brush in the absence of long-ranged interactions. As we increase the grafting density, the minimum in the free energy becomes more pronounced, because the brush-liquid interface becomes more impenetrable, and it shifts to larger film thicknesses as the brush stretches further.

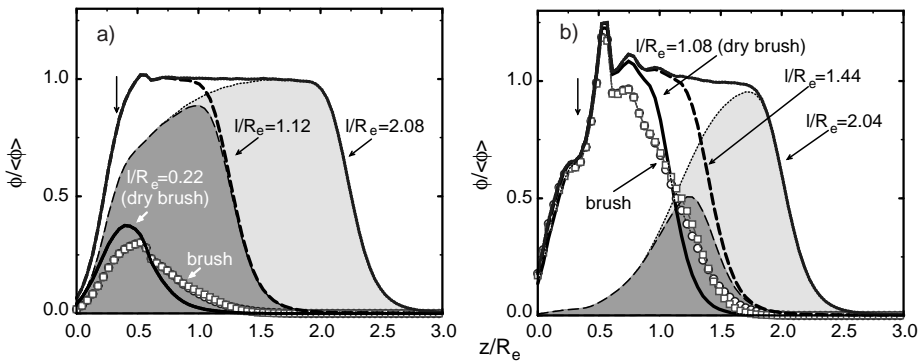


Fig. 2 – Density profiles at intermediate $R_e^2/\Sigma = 0.69$ (a) and high $R_e^2/\Sigma = 3.35$ (b) grafting densities. Film thicknesses are indicated in the key; the lowest value corresponds to a dry brush. The first monomers of the grafted chains are excluded from the profiles, their position is indicated by the vertical arrow. Thick lines present the total density profile $\phi = \phi_g + \phi_f$. For the two larger thickness, lines with symbols represent the profiles of grafted chains and shaded areas correspond to free chains. The values l/R_e in panel (b) are indicated as arrows in fig. 1.

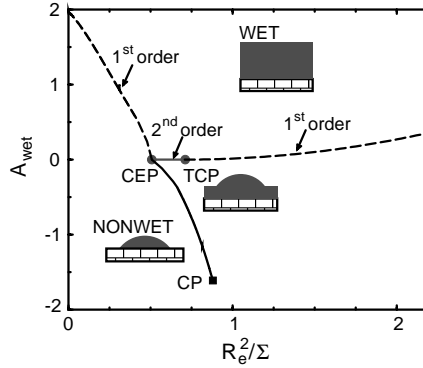


Fig. 3 – Wetting phase diagram in terms of the effective Hamaker constant A_{wet} and the grafting density R_e^2/Σ . Dashed lines denote first-order wetting transitions, the solid curve denotes transitions between a microscopic thin and a mesoscopic thick layer, and the horizontal line at $A_{\text{wet}} = 0$ marks second-order wetting transitions. The line of transitions between a thin and thick layers terminates in a critical end point (CEP) at low grafting densities and in a critical point (CP) at high grafting densities. Second-order and first-order wetting transitions at high grafting densities are separated by a tricritical point (TCP).

A long-ranged interaction A between the substrate and the monomers can induce a wetting transition at arbitrary grafting densities. For low and high grafting densities the liquid does not wet the brush for $A = 0$ and an attractive interaction ($A_{\text{wet}} > 0$) between monomers and substrate is required. The wetting transition is of first order, *i.e.*, upon increasing A the film thickness jumps discontinuously from a very small value ($l < 0.25R_e$) to a macroscopic one. Upon increasing the grafting density R_e^2/Σ we need a smaller (larger) Hamaker constant A_{wet} to bring about wetting at low (high) grafting densities, respectively. At intermediate grafting densities the liquid wets the brush for $A \geq 0$ and there is only a finite liquid layer at negative values of A , which correspond to an effective repulsion between the substrate and the monomers. In the latter case the structure of the brush provides a short-range interaction which favours thick liquid layers, while the long-ranged interactions limit the growth of the liquid layer. Since the short-range interactions decay exponentially with the layer thickness and *all* long-ranged forces are proportional to the Hamaker constant A , the layer thickness diverges logarithmically [20], $l \sim -\ln A$, as we approach the second-order wetting transition at $A_{\text{wet}} = 0^-$. This specific growth law is model dependent, the qualitative wetting behaviour is not. If we described the long-ranged forces between the substrate and the monomers by a potential of the form $-A/z^3 + B/z^4$, the layer thickness would grow like $l \sim 4B/3|A|$ as $A \rightarrow A_{\text{wet}} = 0^-$ [21].

The complete wetting phase diagram is presented in fig. 3. The line of first-order wetting transitions at low grafting densities continues beyond the critical end point (CEP) as a line of first-order transitions between a microscopically thin and a mesoscopically thick liquid layer. As we increase A , the film thickness jumps from thin to thick (*e.g.*, at $R_e^2/\Sigma = 0.697$ and $A = -0.488$ from $l/R_e = 0.26$ to 0.91) and then diverges logarithmically as $A \rightarrow 0^-$. The thin-thick transition stems from the competition of short-ranged and long-ranged forces [22, 23]. Though the transition involves only finite layer thicknesses, the situation is referred to as “frustrated” complete wetting [22–24]. Upon increasing the grafting density the difference in layer thickness between the coexisting phases decreases and the line of first-order transitions terminates in a critical point (CP).

The region of critical wetting transitions at $A_{\text{wet}} = 0$ is bound by the critical end point at small R_e^2/Σ and by a tricritical point (TCP) at high grafting densities. Since the line of

first-order wetting transitions approaches the tricritical point very gradually, the location of the tricritical grafting density could not be determined with high accuracy [25]. The critical point (CP) of the thin-thick transition occurs at a larger grafting density than the tricritical point (TCP), *i.e.*, a thin-thick transition also precedes the first-order wetting transitions in the vicinity of the tricritical point.

Discussion. – Using recent advances in calculating surface and interface properties of polymers in a bad solvent, we have investigated the wetting behaviour of a short chain liquid on a brush of identical segments. We have restricted our calculations to a single temperature and to identical length of the free and grafted chains. Nevertheless, our calculations reveal a rich interplay between grafting density, effective Hamaker constant, and wetting behaviour. Exploring the influence of chain length asymmetry and solvent quality is an interesting subject for future investigations.

At low grafting densities we find first-order wetting transitions analogous to the wetting behaviour at a bare surface. Recent Monte Carlo simulations of the same microscopic model confirm the first-order character of the wetting transition [14]. We expect simulations to verify our results qualitatively, a better description of the packing at the wall is required for accurate quantitative predictions. Upon increasing the grafting density, there are additional attractive interactions for the free chains and a smaller Hamaker constant is required to bring about the wetting transition. We anticipate that the grafted chains laterally aggregate in the dry state [26], a feature which is not captured in our one-dimensional calculations. This will reduce the free energy of the dry state and shift the wetting transition to larger values of the Hamaker constant, however, we do not expect a qualitative change in the wetting behaviour.

Upon increasing the grafting density, we encounter a critical end point. At intermediate grafting densities the liquid wets the brush in the absence of long-ranged forces and there is a second-order wetting transition as the Hamaker constant A approaches zero from below (antagonist forces) [20, 23]. The local free-energy minimum of the dry state at lower grafting densities becomes metastable at $A = 0$ and gives rise to a first-order transition between a thin and a (mesoscopically) thick layer at negative values of the Hamaker constant [27]. This behaviour is analogous to experiments of short alkane chains on water [24, 28, 29], where a transition between a partial wet and a “frustrated” complete wet state, which precedes the second-order wetting transition, is found. Recent experiments study wetting on brushes [30–32] and yield evidence for the stability of a thin and a mesoscopically thick film [30, 31].

The intermediate region of second-order transition terminates in a tricritical wetting transition at larger grafting densities. Beyond, a positive Hamaker constant is required to make the liquid wet the brush and the wetting transition is of first order. This autophobicity of a polymer liquid on a chemically identical brush in the absence of long-ranged attractions has been observed in experiments [3, 12, 13] and in calculations [6, 7, 9, 11].

Our conclusions are partially supported by recent experimental observations. Experiments on oligomeric liquids as well as computer simulations might prove convenient for testing further aspects. In view of the large number of accessible parameters [30] (*e.g.*, solvent quality, relative ratio between chain lengths of grafted and free chains, salt content, or temperature) we anticipate a very rich wetting behaviour. In contrast to fluid-fluid interfaces [28, 29] no experimental realisation of critical wetting for solid-liquid interfaces is known. Our results suggest that by fine tuning of the Hamaker constant this long-sought transition may be observed in wetting experiments on polymer brushes.

Additional remark. – Recent experiments (REITER G. and KHANNA R., *Phys. Rev. Lett.*, **85** (2000) 5599) demonstrate that the free-energy change upon adding free chains on top of a dense brush cannot quantitatively be described by confinement alone. The compressibility

of the liquid has to be taken into account. Our calculations suggest that there is an additional free-energy contribution due to the change of the profile of grafted chains.

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