Roughness-induced fluid interface fluctuations due to polar and apolar interactions

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We investigate substrate roughness-induced fluctuations on liquid films in the presence of polar (exponential) and apolar (van der Waals) interactions in the complete wetting regime. The liquid/vapor interface roughness amplitude σ_w increases rapidly with film thickness ε above a critical thickness ε_c for which the film is stable (or it does not rupture due to presence of polar interactions), and it reaches a maximum at a thickness ε_m slightly larger than ε_c if polar and apolar components are of comparable strength and for small polar potential ranges. As the strength of the polar interaction decreases with respect to the apolar, behavior characteristic of that of apolar interactions within the Derjaguin approximation is recovered for moderate film thicknesses ($\varepsilon > \varepsilon_m$); $\sigma_w \propto \zeta^{-2}$ with ζ the healing length. [S1063-651X(99)11701-X]

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The phenomenon of wetting of fluids on solid substrates has been a long-standing topic of fundamental research for more than a century [1]. Its complexity is cumbersome, since wetting is highly sensitive to roughness and chemical contaminants of the substrates [1–4]. Significant insight into the influence of substrate random roughness has been gained by studies performed within the Derjaguin approximation [2–5]. The latter accounts for replacing the local disjoining pressure Π_d by that of a uniform film of thickness $h(r) - z(r)$ [with $z(r)$ and $h(r)$ being, respectively, the substrate and liquid/vapor surface profile functions] for small substrate roughness amplitudes, and then linearizing the disjoining pressure around the average film thickness ε on a flat surface.

The Lorentzian damping of the Derjaguin approximation [$\propto (1+q^2\zeta^2)^{-1}$] substantially eliminates the small wavelength fluctuations, and the liquid/vapor interface roughness is dominated by the fluctuations at wave vectors $q < 1/\varepsilon$ [1,3]. For a self-affine substrate topology without a natural roughness cutoff (correlation length), the surface is rough at all length scales and the interface follows the substrate morphology at wave vectors $q < 1/\varepsilon$ and $q < 1/\zeta$ (with ζ the healing length that determines the length scale below which fluctuations are damped by the liquid/vapor surface tension γ) [1]. The Derjaguin approximation correctly yields the effective cutoff for $\varepsilon < \zeta$ [1]. Inclusion of nonlocal effects leads to additional exponential damping ($e^{-q\varepsilon}$) of short-wavelength fluctuations [1], while these effects have a small contribution for film thicknesses $\varepsilon < \zeta$ [1,3].

A common case that is usually considered to study the influence of substrate roughness on interface undulations is that of van der Waals interactions [1,7]. These interactions are of fundamental importance in wetting phenomena since they occur universally and fall off more slowly at large distances than other interactions [1,6,8]. The large healing length (thick film) asymptotic behavior of the interface roughness amplitude σ_w follows the power law $\sigma_w \propto \zeta^{-2}$, which is predicted within the Derjaguin framework [9]. Nevertheless, inverse power law potentials do not possess an intrinsic length scale, and thus the film thickness ε is the only length scale that controls the damping of long wavelengths ($q \gg 1/\varepsilon$) [1].

Exponential interactions have been discussed in the context of the wetting transitions, double-layer forces in water solutions against ionizable surfaces, etc. (for a review see de Gennes and co-workers[4]). The exponential potential form and potential effective range λ could have significant impact on the real space fluctuation properties [10]. Recently, a combination of apolar (van der Waals) and polar (simple exponential) interactions was considered to describe rupture of thin films ($\varepsilon < 10$ nm) [11]. The polar component may become significant in systems such as aqueous solutions for small film thicknesses [12]. if we denote by S_{ap} and S_p, respectively, the strength of the apolar and polar component, for $S_{\mathrm{ap}} > 0$ and $S_p < 0$ the apolar component will stabilize the film while the polar component will destabilize (rupture) it [11,12].

However, the actual influence of both interactions (van der Waals and polar exponential) on experimentally measurable interface fluctuation properties (e.g., interface roughness amplitudes by means of x-ray reflectivity) [13] is still missing, and will be the topic of the present work. This will be accomplished by direct calculation of the rms interface roughness amplitude assuming for simplicity self-affine substrate roughness over finite length scales. Our calculations will be confined in the Derjaguin approximation, since the film thickness involved (in the stable film regime) [12] will be large enough to safely ignore contributions due to nonlocal effects for which the contribution falls off exponentially [1,3].

The substrate/liquid and liquid/vapor interfaces are considered random single valued functions of the in-plane position vector $r = (x,y)$ such that $\langle z(r) \rangle = 0$ and $\langle h(r) \rangle = \varepsilon$. For weak interface fluctuations [$|\nabla h(r)| \ll 1$] and in the absence of thermal fluctuations, the interface height profile is given by $\zeta^2 \nabla^2 h(r) = h(r) - z(r) - \varepsilon$, which yields after Fourier transformation [1,3]

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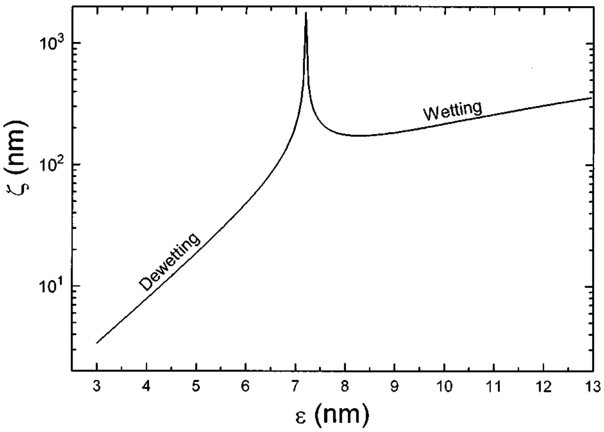

FIG. 1. Healing length ζ vs film thickness ε. A minimum is observed in the wetting or stable regime at $\varepsilon \approx 8.5$ nm.

$$h(q) = (1 + q^2\zeta^2)^{-1} z(q) + \varepsilon\,\delta(q), \tag{1}$$

with the healing length ζ given by $\zeta = [\gamma/(-d\Pi_d(\varepsilon)/d\varepsilon)]^{1/2}$. For the disjoining pressure [11,12]

$$\Pi_d(\varepsilon) = (2S_{\rm ap} d_0^2)\varepsilon^{-3} + (2S_p e^{d_0/\lambda}/\lambda) e^{-\varepsilon/\lambda}, \tag{2}$$

the healing length ζ is given by $\zeta = \{\gamma/[6S_{\rm ap} d_0^2 \varepsilon^{-4} + 2S_p \lambda^{-2} e^{(d_0-\varepsilon)/\lambda}]\}^{1/2}$ with d_0 the Born repulsion length and λ the interaction range of the polar component. For $d\Pi_d/d\varepsilon \geqslant 0$ the film is unstable and rupture occurs, while it is stable for $d\Pi_d/d\varepsilon < 0$. The critical film thickness ε_c below which the instability occurs is defined by $(d\Pi_d/d\varepsilon)_{\varepsilon=\varepsilon_c} = 0$ [12].

Figure 1 shows ζ vs ε for the parameters $d_0 = 0.158$ nm, $\lambda = 0.6$ nm, $S_{\rm ap} = 0.106$ N/m, $S_p = 0.159$ N/m, and $\gamma = 0.0722$ N/m (water) [12]. In the unstable film regime ($\varepsilon < \varepsilon_c \approx 7$ nm) the absolute value of $-d\Pi_d/d\varepsilon (<0)$ is considered, since otherwise ζ will be imaginary. In the stable regime ($\varepsilon > \varepsilon_c$), $-d\Pi_d/d\varepsilon$ has a maximum and subsequently ζ has a minimum at a film thickness ε_m (≈ 8.5 nm) which is assumed to influence the interface fluctuations. Figure 2 shows ζ vs the potential range λ for strong ($S_p \approx S_{\rm ap}$)

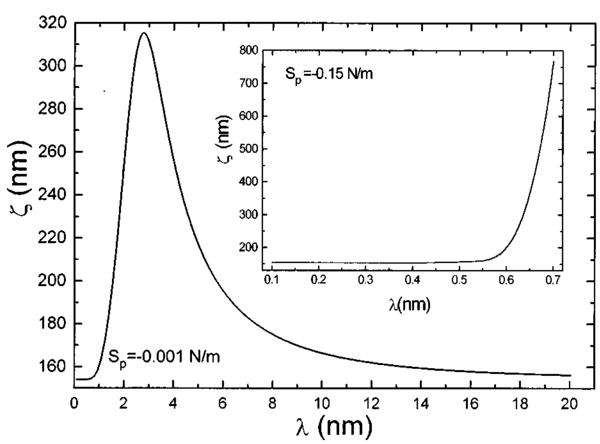

FIG. 2. Healing length ζ vs the polar potential range λ for $d_0 = 0.158$ nm, $\varepsilon = 8.5$ nm, $S_{\rm ap} = 0.106$ N/m, $S_p = -0.159$ N/m (strong polar component), and $\gamma = 0.0722$ N/m. The inset shows ζ vs λ for $S_p = -0.001$ N/m (weak polar component).

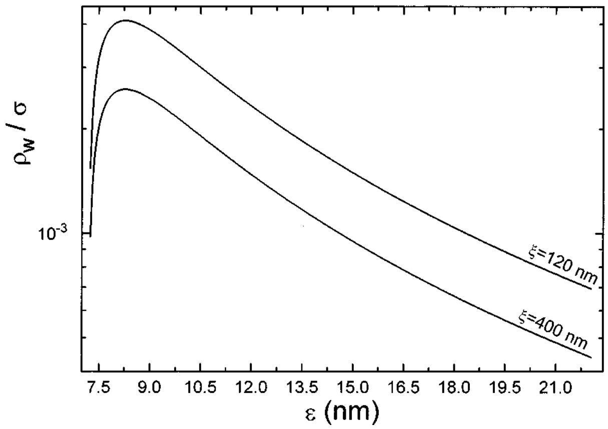

FIG. 3. Local interface slope ρ_w/σ vs film thickness ε for $d_0 = 0.158$ nm, $\lambda = 0.6$ nm, $S_{\rm ap} = 0.106$ N/m, $S_p = -0.159$ N/m, $\gamma = 0.0722$ N/m, $a_0 = 0.3$ nm, $\sigma = 1$ nm, $H = 0.4$, and ξ as indicated. The local slope shows a maximum at the minimum of the healing length ζ as a function of the film thickness ε.

and weak ($S_p \ll S_{\rm ap}$) polar interactions. In the first case ζ increases monotonously with λ, while in the second case it shows a maximum as a function of the potential range λ.

The substrate roughness will be modeled as a self-affine fractal, which is observed in a wide variety of thin solid films [14]. Besides the correlation length ξ, the substrate fluctuations are characterized by the rms amplitude σ, and the roughness exponent H ($0 < H < 1$) which is a measure of the degree of surface irregularity at short length scales [14,15]. For self-affine surfaces, $\langle |z(q)|^2 \rangle$ scales as [14]

$$\langle |z(q)|^2 \rangle \propto \begin{cases} q^{-2-2H} & \text{if } q\xi \gg 1 \\ \text{const} & \text{if } q\xi \ll 1. \end{cases} \tag{3}$$

The Lorentzian model $\langle |z(q)|^2 \rangle = [A/(2\pi)^5]\sigma^2\xi^2(1 + aq^2\xi^2)^{-1-H}$ interpolates in a simple manner between the asymptotic limits defined by Eq. (3). The parameter a is defined by $a = (1/2H)[1 - (1 + aQ_c^2\xi^2)^{-H}]$ with $Q_c = \pi/a_0$ (a_0 is the atomic spacing), and A is the macroscopic average flat area. Although we will restrict our presentation to a specific substrate roughness exponent H in the mean field regime $H < \frac{1}{2}$ [1,2], similar results will hold for other values of H as far as the effect of the interaction potential form is concerned. This is because H will influence mainly the magnitude of the interface amplitude [9]. In any case, finite length scale roughness (finite ξ) is necessary for the correct determination of the liquid interface fluctuation properties.

First, we will comment on the weak fluctuation regime since Eq. (1) applies for weak interface local slopes $\rho_w \equiv \langle |\nabla h|^2 \rangle^{1/2} \ll 1$ ($|\nabla h| \ll 1$) [1,2,16], and small local variations of the film thickness in comparison with the mean thickness ε [1]. Substituting the Fourier transform $h(r) = \int h(q) e^{-i\mathbf{q}\cdot\mathbf{r}} d^2\mathbf{q}$ in ρ_w and considering translation invariant interfaces or $\langle h(q)h(q') \rangle = [(2\pi)^4/A]\langle |h(q)|^2 \rangle \delta^2(q + q')$, we obtain

$$\rho_w = \left([(2\pi)^4/A] \int_{0<q<Q_c} q^2 \langle |h(q)|^2 \rangle d^2\mathbf{q} \right)^{1/2}. \tag{4}$$

Figure 3 shows ρ_w as a function of the mean film thickness

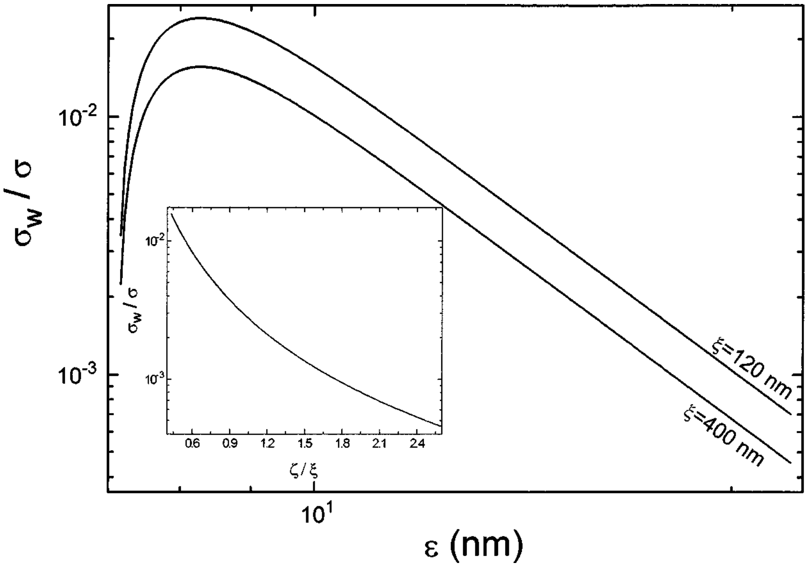

FIG. 4. Interface roughness amplitude σ_w/σ vs film thickness ε for $d_0 = 0.158$ nm, $\lambda = 0.6$ nm, $S_{\mathrm{ap}} = 0.106$ N/m, $S_p = -0.159$ N/m, $\gamma = 0.0722$ N/m, $a_0 = 0.3$ nm, $\sigma = 1$ nm, $H = 0.4$, and ξ as indicated. σ_w/σ shows a maximum at the minimum of the healing length ζ as a function of ε (Fig. 1). The inset depicts directly σ_w/σ vs the healing length ζ.

ε. The local slope shows a maximum at the film thickness ε_m, where ζ has a minimum in Fig. 1, while it decreases with increasing ξ, reflecting the smoothing of substrate roughness at long wavelengths, thus inducing weaker interface fluctuations. For thickness $\varepsilon > \varepsilon_m$ the effect of ξ is rather uniform, while for $\varepsilon_c < \varepsilon < \varepsilon_m$ as ε approaches ε_c (unstable regime) it becomes negligible, since ζ grows larger more quickly than ξ. In any case, in the stable film regime ($\varepsilon > \varepsilon_c$) the local slope is small $\rho_w (\ll 1)$ as long as σ is small $(\sigma/\xi \ll 1)$, justifying the applicability of the linear treatment.

Furthermore, we will investigate to what degree the associated to roughness spectrum $\langle |h(q)|^2 \rangle$ real space fluctuation properties (which can be measured experimentally [13]) still keep a strong signature from the extremum behavior of the healing length ζ in the stable film regime $(\varepsilon > \varepsilon_c)$. For this purpose, we will examine the behavior of the interface roughness amplitude σ_w as a function of film thickness ε for $\varepsilon > \varepsilon_c$. This roughness parameter is given by [13]

$$\sigma_w = \left([(2\pi)^4/A] \int_{0<q<Q_c} \langle |h(q)|^2 \rangle d^2\mathbf{q} \right)^{1/2}, \tag{5}$$

and Fig. 4 depicts σ_w/σ vs ε for $\varepsilon > \varepsilon_c$. Similar to the local interface slope, the interface amplitude σ_w shows a maximum at the film thickness ε_m, where ζ has a minimum, while with further increase of the film thickness the power law behavior $\sigma_w \sim \zeta^{-2}$ associated with the Derjaguin approximation [9] is recovered. Increment of the roughness correlation length ξ has an effect similar to that observed for ρ_w. Nevertheless, the effect of substrate roughness on the rms interface amplitude is more pronounced in absolute magnitude than that of the local slope as ε approaches ε_c. The inset of Fig. 4 depicts the direct dependence of σ_w on the correlation length ξ relative to the healing length ζ. The interface amplitude decreases drastically in the regime $\zeta \gg \xi$, indicating strong damping of substrate-induced fluctuations at length scales beyond which substrate roughness saturates [Eq. (3); $\langle |z(q)|^2 \rangle \propto$const for $q\xi \ll 1$] [9].

Figure 5 depicts the dependence of σ_w/σ on film thickness for various polar coefficients S_p. The transition from the extremum behavior (maximum) for comparable polar and apolar components ($S_p \approx S_{\mathrm{ap}}$) to that dominated by apolar (van der Waals) interactions occurs rather fast at moderate film thicknesses. With increasing film thickness the crossover to the power law regime $\sigma_w \sim \zeta^{-2}$ [7,9] occurs rather rapidly for film thicknesses ε slightly larger than ε_m, which is determined for comparable polar and apolar components ($S_p \approx S_{\mathrm{ap}}$) and small polar potential ranges ($\lambda < 1$ nm). The fluctuation properties, however, depend on polar component strength S_p in such a way that they differ by more than an order of magnitude when comparing the strong polar regime ($S_p \approx S_{\mathrm{ap}}$) to the weak polar regime ($S_p \ll S_{\mathrm{ap}}$).

Figure 6 shows the dependence of the interface amplitude σ_w on the polar potential range λ. The interface amplitude remains rather insensitive for small polar ranges λ, showing a plateau which increases with increasing polar strength S_p, followed by a steep decrease with further increment of the polar potential range. For weak polar interactions ($S_p \ll S_{\mathrm{ap}}$), an extremum behavior of σ_w/σ develops for larger λ which is characterized by a minimum and a slow increment of σ_w with further increment of the potential range λ. Such behavior can be understood from Fig. 2, where especially for

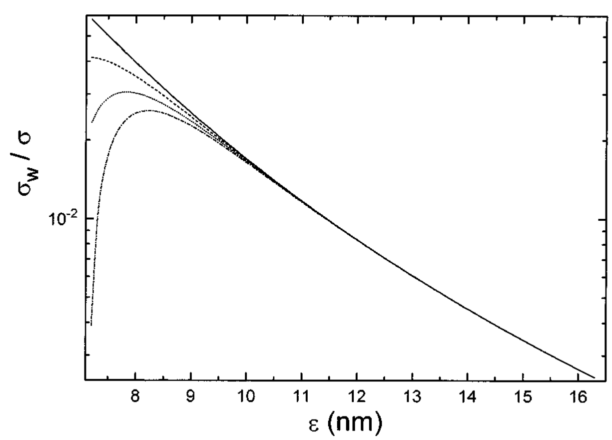

FIG. 5. Interface roughness amplitude σ_w/σ vs film thickness ε for $d_0 = 0.158$ nm, $\lambda = 0.6$ nm, $S_{\mathrm{ap}} = 0.106$ N/m, $\gamma = 0.0722$ N/m, $a_0 = 0.3$ nm, $\sigma = 1$ nm, $H = 0.4$, and $\xi = 100$ nm. Solid line, $S_p = -0.001$ N/m; dashes, $S_p = -0.05$ N/m; dots, $S_p = -0.1$ N/m; dot-dashed line, $S_p = -0.15$ N/m.

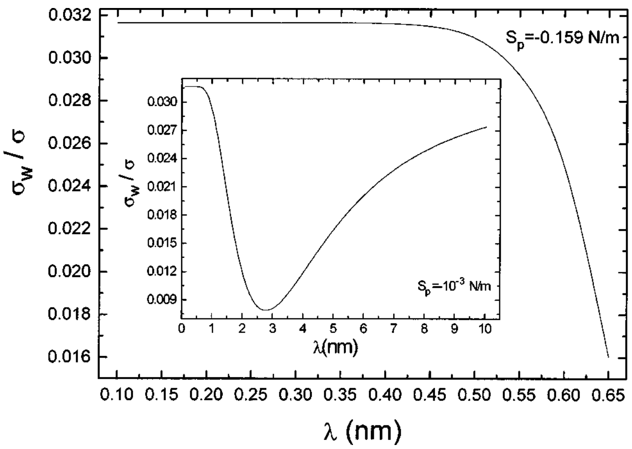

FIG. 6. Interface roughness amplitude σ_w/σ vs polar potential range λ for $d_0=0.158$ nm, $\varepsilon=8.5$ nm, $S_{\mathrm{ap}}=0.106$ N/m, $S_p=-0.159$ N/m, $\gamma=0.0722$ N/m, $a_0=0.3$ nm, $\sigma=1$ nm, $H=0.4$, and $\xi=100$ nm. The inset shows a similar schematic for $S_p=-0.001$ N/m (weak polar interactions).

weak polar interactions (inset), the healing length shows a maximum that is followed by a slow decrement. This dependence is reflected on σ_w/σ, however, with a minimum instead of a maximum since larger ζ corresponds to smaller influence of the substrate undulations (inset of Fig. 4; smoothing due to surface tension at larger length scales). For strong polar interactions, ζ increases monotonously with λ, which is reflected in Fig. 6 by the monotonous decrement of the interface roughness amplitude σ_w/σ.

In conclusion, we investigated real space fluctuation properties of liquid films in the complete wetting of self-affine rough substrates, in the presence of apolar (stabilizing) and polar interactions (which lead to destabilization or rupture of the liquid film below some critical thickness). The interface rms amplitude and local slope show a maximum at small film thickness for polar and apolar components of comparable strength and small polar potential ranges. As the strength of the polar component becomes smaller than that of the apolar, the behavior of the fluctuation properties that was found within the Derjaguin approximation is recovered for rather moderate film thicknesses. Finally, the interface roughness amplitude develops a complex dependence on the polar potential range for weak polar interactions.

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