Fluid interface fluctuations within the generalized Derjaguin approximation

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The fluctuation properties of fluid interfaces bounded by rough surfaces are investigated within a linear generalization of the Derjaguin approximation. In the thick-film regime, the interface roughness amplitude is lower in magnitude from that obtained in the Derjaguin approximation. Nevertheless, for large healing lengths ζ the power-law asymptotic behavior $\sigma_w \sim \zeta^{-2}$, which is observed in the Derjaguin approximation, is still preserved. Moreover, the rms local interface slope ρ is shown to attain small values for film thicknesses larger than the substrate roughness amplitude and to follow an asymptotic power-law behavior $\rho \sim \zeta^{-2}$ for large ζ. [S0163-1829(97)07436-5]

Wetting phenomena of fluids on solid substrates have been an important topic of applied and fundamental research for more than a century. However, the understanding of the complexity of these phenomena is still incomplete, since wetting is highly sensitive to roughness and chemical contaminants of the solid substrates.[1–4] In general, these types of surface disorder can have a dramatic influence on interfacial processes which are of experimental and technological interest.

Various theoretical treatments[2–4] of the influence of surface roughness on the wetting properties of liquids have been performed within the so-called Derjaguin approximation.[5] In fact, this approximation accounts for replacing the local disjoining pressure Π_d by that of a uniform film of thickness $h(r)-z(r)$ [$z(r)$ and $h(r)$ are, respectively, the substrate and liquid-vapor surface/interface profile functions] for small substrate roughness amplitudes, and then linearize the disjoining pressure around the average film thickness ε that would exist on a flat surface.[3] The average thickness ε is given by the relation $\Delta\mu = \Pi_d(\varepsilon)$, with $\Delta\mu$ the chemical potential difference between the liquid and vapor phases, and the liquid-vapor interface fluctuations are described by the equation $\varsigma^2\nabla^2 h = h - z - \varepsilon$ or $h(q) = (1+q^2\xi^2)^{-1} z(q) + \varepsilon\,\delta(q)$ in Fourier space. ζ is the healing length which characterizes the competition between surface tension and disjoining pressure.

The Derjaguin approximation excludes damping of short-wavelength fluctuations due to averaging of the contribution to the local disjoining pressure. The damping (nonlocal) effect was taken into account initially in terms of a linear approach, while nonlinear effects were investigated extensively for periodically corrugated surfaces.[1] In general, the nonlocal effects are expected to have a small contribution for film thickness smaller than the healing length ($\varepsilon < \zeta$), and for $z(q)$ relatively large at wave vectors $q\varepsilon < 1$.[1,3] In this case, the Lorentzian damping (the main damping in the Derjaguin approximation) substantially eliminates the small-wavelength fluctuations, and the liquid roughness is dominated by the fluctuations at $q\varepsilon < 1$.[1]

For self-affine substrate roughness, the investigations were limited only to power-law roughness, neglecting the existence of any natural roughness cutoff (correlation length).[1] In this case, since the surface is considered rough at all length scales and the interface follows the substrate morphology at wave vectors $q\zeta < 1$ and $q\varepsilon < 1$, the Derjaguin approximation gives the effective cutoff ($q\zeta < 1$ if $\varepsilon < \zeta$) correctly.[1] Moreover, an investigation of the linear expansion of the local disjoining pressure Π_d was performed using for simplicity the Derjaguin result for the interface spectrum $h(q)$,[1] and results similar to those observed in other studies (regarding the weak and strong fluctuation regime) (Ref. 2) were obtained. Nevertheless, the precise extent that the linear generalization of the Derjaguin approximation influences real-space interface fluctuation properties (i.e., roughness amplitudes) induced by self-affine substrate roughness over finite length scales (finite correlation length) was not explored.

Experimentally, simultaneous measurement of the roughness of the solid-liquid and liquid-vapor interfaces can be performed by grazing-incidence x-ray scattering.[6] Indeed, results for cyclohexane films on silicon wafers[7] seemed to be in good agreement with the predictions within the Derjaguin scheme.[3] Therefore, the actual effect of the linear generalization of the Derjaguin approximation[1] on experimentally accessible real-space interface fluctuation properties (induced by substrate imperfections) requires a more detailed investigation. Comparison with the results obtained within the Derjaguin framework will be sufficient to determine the regime of film thicknesses where significant deviations possibly occur. Moreover, since the calculations will be restricted in the weak fluctuation regime or small local interface slope ($|\nabla h| \ll 1$), the behavior of the latter as function of characteristic system parameters will be thoroughly investigated.

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 $\langle h(r)\rangle = \varepsilon$. The difference in free energies of the two interfaces is given by[1]

$$F = \int [(\gamma_{\mathrm{SD}} - \gamma_{\mathrm{SV}})(1+|\nabla z|^2)^{1/2} + \gamma(1+|\nabla h|^2)^{1/2} + P(h) + \Delta\mu(h-z)]\,d^2r, \tag{1}$$

with γ_{SV}, γ_{SL}, and γ, respectively, the solid-vapor, solid-liquid, and liquid-vapor surface tensions. The term $P(h)$ is the interaction per unit area of the solid-liquid surfaces, and is determined by the long-range tails of the interaction potential $U(r,z)$. The latter is described by pair interactions between the molecules of all phases. Finally, the term $\Delta\mu(h-z)$ is the chemical potential difference between liquid and vapor phases integrated over the film volume. Furthermore, minimization of the free energy for weak fluctuations ($|\nabla h(r)|\ll 1$) in the absence of thermal fluctuations yields in real and Fourier space,[1,3] equivalently,

$$\varsigma^2\nabla^2 h(r)=[h(r)-\varepsilon]-\int K(r-p)z(p)d^2p,$$

$$h(q)=K(q)(1+q^2\varsigma^2)^{-1}z(q)+\varepsilon\,\delta(q), \qquad (2)$$

with $\zeta=[\gamma/\int U(r,\varepsilon)d^2r]^{1/2}$ the healing length which determines the length scale below which short-wavelength fluctuations are damped by the liquid-vapor surface tension γ.

The function $K(r)$ is given by $K(r)=U(r,\varepsilon)/\int U(r,\varepsilon)d^2r$. In the Derjaguin approximation $K(r)\sim\delta(r)$, which yields effectively $K(q)=1$.[2,3] Furthermore, for long-range inverse power-law interactions of the form $U(R)=C\pi^{-2}R^{-2n-2}$ ($n\geqslant 1$; van der Waals interactions) with $R=(r^2+z^2)^{1/2}$,[1,8] we obtain and in real and Fourier space, respectively,

$$K(r)=(n/\pi)\varepsilon^{2n}(r^2+\varepsilon^2)^{-1-n},$$

$$K(q)=[2/\Gamma(n)](q\varepsilon/2)^n K_n(q\varepsilon), \qquad (3)$$

with the healing length given by $\zeta=(n\pi\gamma/C)^{1/2}\varepsilon^n$. In fact, van der Waals interactions are of fundamental importance in wetting phenomena since they occur universally and fall off more slowly at large distances than other interactions.[1] The special case of $n=2$ corresponds to the nonretarded van der Waals interactions,[8] where we will base for simplicity our subsequent calculations. In Eq. (3), $\Gamma(n)$ is the gamma function, and $K_n(x)$ the second kind Bessel function which for $q\varepsilon\gg 1$ yields the exponential asymptotic behavior of $K(q)$: $K(q)\approx[\pi^{1/2}/\Gamma(n)](q\varepsilon/2)^{n-1/2}e^{-q\varepsilon}$.

The substrate roughness will be modeled as self-affine roughness, which is observed in a wide variety of thin solid film surfaces.[9,10] The roughness fluctuations $z(r)$ are characterized by the rms roughness $\sigma=\langle z(r)^2\rangle^{1/2}$, the in-plane correlation length ξ which is a measure of the average distance between consecutive hills or valleys, and the roughness exponent $H(0<H<1)$ which measures the degree of surface irregularity.[9,10] For self-affine surfaces, the roughness spectrum $\langle|z(q)|^2\rangle$ can be modeled for simplicity by the analytic form[11]

$$\langle|z(q)|\rangle=[A/(2\pi)^5]\sigma^2\xi^2(1+aq^2\xi^2)^{-1-H}, \qquad (4)$$

which interpolates between the self-affine asymptotic limits $\langle|z(q)|^2\rangle\propto q^{-2-2H}$ if $q\xi\gg 1$, and $\langle|z(q)|^2\rangle\propto$const if $q\xi\ll 1$.[9,10] A is the macroscopic average flat area, and $Q_c=\pi/a_o$, with a_o to the order of the atomic spacing. The parameter a in Eq. (4) is given by $a=(1/2H)[1-(1+aQ_c^2\xi^2)^{-H}]$ if $H>0$, and $a=\frac{1}{2}\ln(1+aQ_c^2\xi^2)$ if $H=0$ (logarithmic roughness[11]).

Our numerical calculations were performed for $n=2$ (nonretarded van der Waals interactions) with $\gamma=70\times 10^{-14}$ erg/nm^2,[12] and $C\approx 6\times 10^{-14}$ erg.[13] The roughness exponent $H(0\leqslant H<1)$, and the parameters σ and ξ were based mainly on values arising from experimental investigations of thin solid film nanoscale roughness over a wide range of systems (e.g., Ag, Au), where the self-affine structure usually appears during nonequilibrium film growth.[10]

Initially, we will comment on the weak-fluctuation regime where the present linear treatment applies. Equation (2) was derived under the assumption of weak interface fluctuations ($|\nabla h(r)|\ll 1$) for which an effective measure is the rms local interface slope[14] which is given by the expression $\rho=\langle|\nabla h|^2\rangle^{1/2}$. Upon substitution of the Fourier transform of $h(r)=\int h(q)e^{-iq\cdot r}d^2q$, we obtain

$$\rho=\left\{-\int(qq')\langle h(q)h(q')\rangle e^{-i(q+q')\cdot r}d^2q\,d^2q'\right\}^{1/2}. \qquad (5)$$

For statistically stationary surfaces up to second order (translation invariance), the product $\langle h(q)h(q')\rangle$ is given by

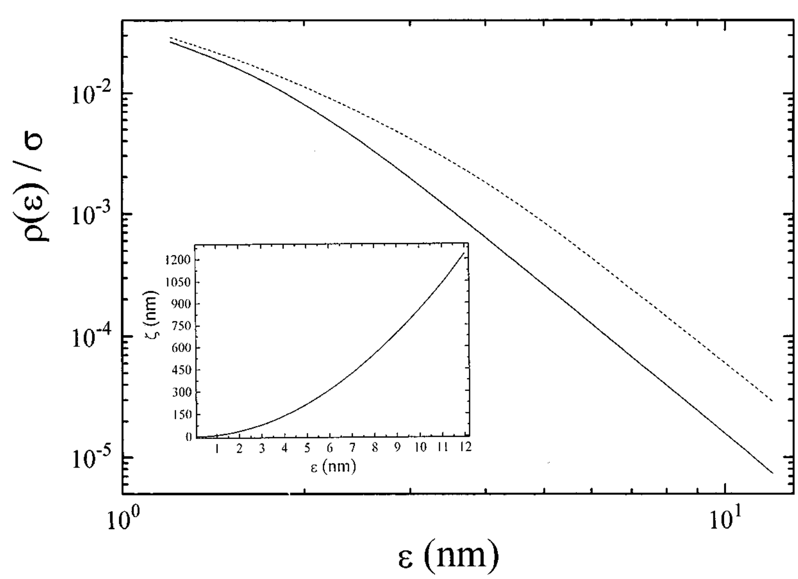

FIG. 1. Schematics of local interface slope $\rho(\varepsilon)$ vs ε for $a_0=0.3$ nm, $\sigma=1$ nm, $\xi=40$ nm, $n=2$, and $H=0.7$: $K(q)\neq 1$ (solid line) and $K(q)=1$ (dashes). The linear regime in both cases corresponds to the power-law asymptotic behavior $p\sim\varepsilon^{-2n}$. The inset shows the film thickness ε vs the healing length ζ for $n=2$.

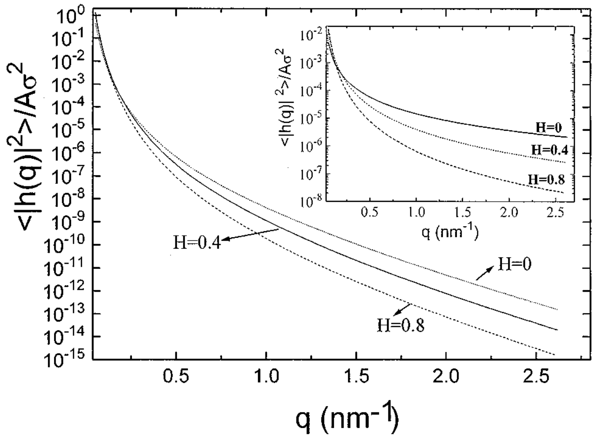

FIG. 2. Schematics of $\langle |h(q)|^2\rangle$ vs $q[K(q)\neq 1]$ for $a_0 = 0.3$ nm, $\xi = 40$ nm, $n=2$, $\varepsilon = 2$ nm, and various values of H (=0, 0.4, and 0.8). The inset shows $\langle |h(q)|^2\rangle$ vs q in the Derjaguin approximation $[K(q)=1]$ for various values of H (=0, 0.4, and 0.8).

$\langle h(q)h(q')\rangle = [(2\pi)^4/A]\langle |h(q)|^2\rangle \delta^2(q+q')$. Upon substitution in Eq. (5), we obtain

$$\rho = \left\{ [(2\pi)^4/A] \int_{0<q<Q_e} q^2 K(q)^2 \times (1+q^2 \varsigma^2)^{-2} \langle |z(q)|^2\rangle d^2 q \right\}^{1/2}, \tag{6}$$

with $\rho \sim \sigma$ since $\langle |z(q)|^2\rangle \sim \sigma^2$. Since $K(q) \leqslant 1$ [Eq. (3)], the local slope ρ in the Derjaguin approximation $[K(q)=1]$ will yield an upper bound for any film thickness ε.

Numerical calculations of the rms local slope are shown in Fig. 1. The inset shows the healing length ζ vs ε for the particular parameters C and γ. In fact, the assumption of weak fluctuations is fulfilled up to very low thicknesses $\varepsilon \approx \sigma$ assuming σ to be small. Indeed, numerical solutions of the nonlinear version of Eq. (2) have shown that the liquid interface follows the substrate fluctuations closely even up to thicknesses $\varepsilon \approx \sigma$ where the linear scheme[1] is no longer valid. The low value of the local interface slope for small σ at $\varepsilon \approx \sigma$ is consistent with such behavior, since it implies the applicability of the linear approximation rather closely to its limit of validity. For large healing lengths $\zeta \gg \xi$, we expect $\rho \ll 1$ intuitively, since the damping caused by the interface elastic properties occurs at wavelengths much longer than those where substrate roughness shows significant structure $(q > 1/\xi)$. Thus interface roughness induced from the substrate is expected to be rather small and decreasing with increasing healing length. For large healing lengths $\zeta \gg \xi$ (equivalently large film thicknesses since $\zeta \sim \varepsilon^n$), the local slope follows the asymptotic power-law behavior $\rho \sim \varsigma^{-2}$ or equivalently $\rho \sim \varepsilon^{-2n}$ for $K(q)\neq 1$ and $K(q)=1$ (the linear regime in Fig. 1).

Figure 2 shows $\langle |h(q)|^2\rangle$ vs q for various values of H and $K(q)\neq 1$. The inset depicts similar plots but for $K(q)=1$ (Derjaguin approximation). As can be observed, the effect of H is significantly suppressed in the generalized case due to the exponential damping $K(q) \propto e^{-q\varepsilon}$ of the short-wavelength fluctuations. Figure 3 depicts the effect of the

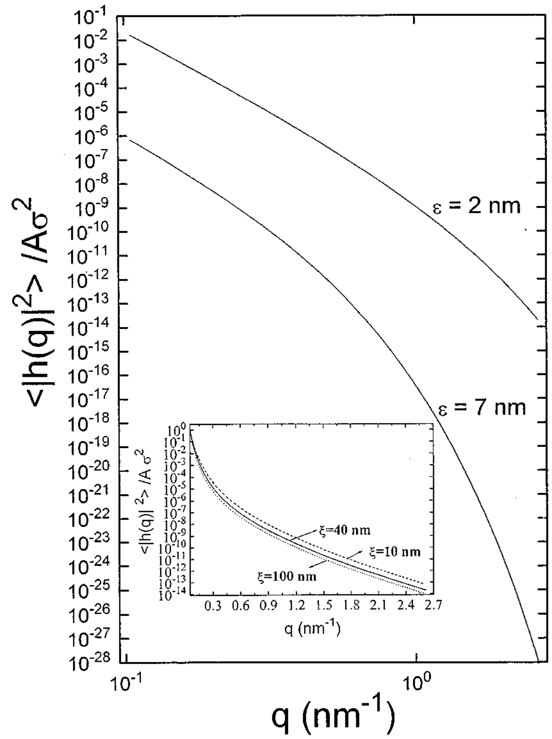

FIG. 3. Schematics of $\langle |h(q)|^2\rangle$ vs $q[K(q)\neq 1]$ for $a_0 = 0.3$ nm, $\xi = 40$ nm, $n=2$, $H=0.4$, and two different values of the film thickness ε (=2 and 7 nm). The inset shows $\langle |h(q)|^2\rangle$ vs $q[K(q)\neq 1]$ for $a_0 = 0.3$ nm, $\varepsilon = 2$ nm, $n=2$, $H=0.4$, and various values of ξ (=10, 40, and 100 nm).

liquid film thickness ε on $\langle |h(q)|^2\rangle$, and the inset the effect of the substrate correlation length ξ. Therefore, as the plots indicate, the generalization of the Derjaguin approximation leads to drastic effects on $\langle |h(q)|^2\rangle$.[1,3] Nevertheless, it remains an open question to what degree the $\langle |h(q)|^2\rangle$ real-space fluctuation properties associated to the roughness spectrum continue to keep a strong signature from these drastic effects.

For this purpose, we will examine the behavior of the liquid interface rms roughness, and we will compare it to that calculated in the Derjaguin approximation. The rms roughness amplitude of the liquid-vapor interface from flatness is given by[11,15]

$$\sigma_w = \left\{ [(2\pi)^4/A] \int_{0<q<Q_e} K(q)^2 \times (1+q^2 \varsigma^2)^{-2} \langle |z(q)|^2\rangle d^2 q \right\}^{1/2}. \tag{7}$$

In general, since $K(q) \leqslant 1$, the roughness amplitude σ_w will be lower than that in the Derjaguin approximation. Figure 4 shows σ_w/σ vs ε for $K(q)\neq 1$ and $K(q)=1$. For significantly large film thicknesses σ_w/σ approaches the regime of the asymptotic power-law behavior $\sigma_w/\sigma \propto \varepsilon^{-2n}$ or $\sigma_w/\sigma \propto \zeta^{-2}$ (since $\zeta \sim \varepsilon^n$), which was observed previously within the Derjaguin approximation.[15] However, for $K(q)\neq 1$ the power-law regime is approached at a faster rate with increasing film thickness ε. As Fig. 4 indicates, the main effect of the generalized Derjaguin approximation on the rms interface roughness is revealed in the thick-film regime or ratios

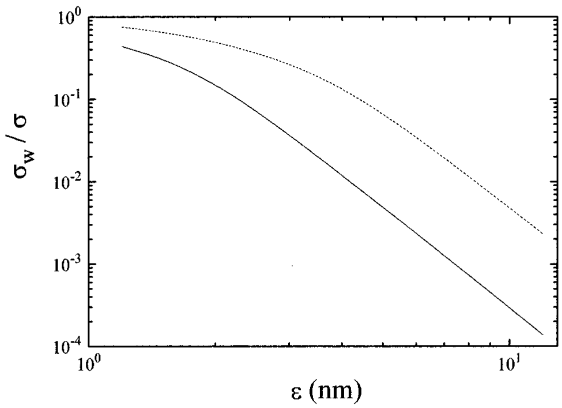

FIG. 4. Schematics of σ_w/σ vs ε for $a_0=0.3$ nm, $\xi=40$ nm, $n=2$, and $H=0.7$: solid line $K(q)\neq 1$, and dashes $K(q)=1$. The linear regime in the log-log plot corresponds to the asymptotic power-law behavior $\sigma_w/\sigma \propto \varepsilon^{-2n}$.

$\varepsilon/\xi>0.1$ (in the present case). Moreover, remarks similar to those for σ_w also hold for the height-height correlation function $C_w(r)\propto\int\langle|h(q)|^2\rangle e^{-iq\cdot r}d^2q$. This is expected since the maximum of $Cw(r)$ is σ_w^2 which clearly depicts the significance of the exponential damping of the short-wavelength fluctuations.

Finally, we should point out that in a real system thermal fluctuations will contribute an additional roughness to that induced from the substrate, and should be taken rigorously into account.[2] However, for sufficiently low temperatures and/or small healing lengths, interface fluctuations induced from substrate roughness can dominate those which are thermally induced.[15] Thus, since the higher-order contributions to the Derjaguin approximation lead to lower roughness amplitudes, thermally induced fluctuations will have a stronger effect on the interface fluctuations than that predicted in earlier studies within the Derjaguin framework.

In conclusion, in our study we investigated the effects of the generalization of the Derjaguin approximation on fluctuation properties of liquid films that completely wet self-affine rough substrates. From our calculations we can infer that higher-order corrections to the Derjaguin approximation could yield a significant contribution to the real-space fluctuation properties of the liquid-vapor interface in the weak-fluctuation regime. For sufficiently thin films the Derjaguin and linear approximations agree well, which is also found in agreement with numerical results on periodically rough surfaces.[1] Although, at large film thicknesses (or $\zeta\gg\xi$) the Derjaguin approximation breaks down, this failure may not be important since the liquid surface is nearly flat ($\sigma_w/\sigma \ll 1$). Nevertheless, the large healing length ($\zeta\gg\xi$) asymptotic behavior of the interface rms roughness amplitude σ_w predicted in the Derjaguin approximation ($\sigma_w \sim\zeta^{-2}$) is still preserved. The latter is in agreement with similar predictions in former studies.[1] Moreover, the weak-fluctuation regime (where the linear treatment applies) is characterized by a rms local interface slope ρ which is proportional to the substrate rms roughness amplitude σ, and has an asymptotic power-law behavior at large healing lengths ($\zeta\gg\xi$); $\rho\sim\zeta^{-2}$.

Although we choose to work with an interaction potential without any intrinsic length scale [in contrast to exponentially decaying potentials $U(r)\sim e^{-ar^n}$ with $n=1$ and 2],[1] qualitatively similar behavior is expected with a crossover to surface-tension-dominated regime ($q\varepsilon>1$) to occur at smaller film thicknesses.[16] However, the precise extent to which the potential form alters the behavior of the interface fluctuation properties will be encountered in future studies.

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