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WETTING ON ROUGH SURFACES

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Abstract—This paper concentrates on effects of roughness on the wettability. Surface roughness is described by an rms amplitude Δ, a correlation length ξ, and a roughness exponent H ($0<H<1$). It is shown that the apparent contact angle depends critically on the roughness exponent H and long wavelength ratio Δ/ξ. For a contact angle θ determined by Young's equation, smaller than a certain transition angle θ_{tr}, the apparent contact angle decreases with increasing roughness and vice versa for $\theta>\theta_{tr}$. The transition angle θ_{tr} appears to be smaller than 90°, and decreases with increasing roughness exponent H.

Keywords: Critical phenomena; Theory; Thin films; Interface; Surface

1. INTRODUCTION

Wetting of liquids on solid surfaces is a topic of fundamental interest with widespread technological implications [1–5]. Examples include coating technology, thin film technology but also gluing and lubrication. For flat solid surfaces the notion of capillarity provides the principal key for the description of wetting phenomena by using physical concepts of interfacial surface tension $\sigma_{\alpha\beta}$ between two different phases α and β. If σ_{sv}, σ_{sl}, and σ_{lv} are the solid–vapor, solid–liquid and liquid–vapor interfacial surface tensions, respectively, a liquid droplet will wet the solid surface if $\sigma_{sv}-(\sigma_{sl}+\sigma_{lv})>0$ (complete wetting), while if $\sigma_{sv}-(\sigma_{sl}+\sigma_{lv})<0$ partial wetting occurs leading to a non-zero contact angle θ at the junction of solid–liquid–vapor. The latter is given by Young's equation, namely $\cos\theta=(\sigma_{sv}-\sigma_{sl})/\sigma_{lv}$ [1–5]. $\sigma_{\alpha\beta}$ represents the force needed to stretch an interface by a unit distance or equivalently, the energy necessary to create a unit surface area of an $\alpha\beta$ interface, provided that the mechanical distortions and strains are negligibly small in the case of σ_{sv}. In principle the Young's equation applies only to one-dimensional spreading and becomes invalid if the substrate is not rigid and motion of the contact-line takes place in both horizontal and vertical directions. The force equilibrium ignores the vertical component of the surface tension which acts along the line of contact. As the capillary forces are not balanced, external forces must be applied to the solid to achieve equilibrium. These forces may produce even deformation in highly deformable solids, such as gels and rubber, destroying the co-planarity of interfacial tensions that is assumed in Young's equation and causing ridge formation at the interfacial region. With the use of the Young's equation, it has to be stressed that only a "quasi-equilibrium" exists within the window of time when observations are made, provided that the solids deformation rate is small. However, wetting of solid surfaces is extremely sensitive to surface geometrical/chemical (roughness/contaminants) disorder which manifests itself by the contact angle hysteresis phenomenon [1–5].

In earlier models of geometrical disorder [6], the case of periodic roughness $h(x)=h_o\sin(2\pi x/\lambda)$ was considered. An apparent contact angle, $\theta_g\cong\theta-(dh/dx)$, if $h_o/\lambda<1$ was defined with respect to the average solid surface in the case of a contact line parallel to the grooves (allowing local application of Young's equation). The maximum advancing or receding apparent contact angle was found to be $\theta_g\cong\theta\pm(2\pi h_o/\lambda)$. This model predicts a hysteresis of the contact angle when the contact line is parallel to the grooves. However, if a finite angle exists between the contact line and the groove, the problem is translation invariant in the direction perpendicular to the grooves excluding any hysteresis [3–5]. In addition, the translational invariance along the contact line implies that when it jumps from one to another groove it does that as a whole, while experimentally

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only finite portions of the contact line are shown to participate in these jumps [3–5, 7]. Finally, the models assuming grooves in a perpendicular direction show a hysteresis in an infinite but countable number of directions [8, 9]. It implies that hysteresis in all directions can only occur if random roughness is present on the surface.

Based on a thermodynamic analysis, Wenzel [10] introduced an apparent contact angle θ_w, where $\theta_w = \cos^{-1}(D_r\cos\theta)$ and D_r represents the ratio of the average area of the actually attached interface to its projected part. In his approach the rough surface was supposed to be completely wetted and unwetted sharp grooves were ignored. A similar model was proposed by Cassie and Baxter [11] taking into account the area fraction D_f of an un-contacted solid–liquid interface on the solid. Unfortunately neither of these theories can predict correctly the experimental contact angles [12]. Further, the parameters D_r and D_f are not easily experimentally accessible. Moreover, the corresponding equations are only correct for radial grooves with a liquid droplet spreading radially, for which an equilibrium state can be reached [12]. Wenzel's equation predicts that with increasing roughness the apparent contact angle θ_w decreases for $\theta<90°$, while θ_w increases for $\theta>90°$. In other words a transition occurs for theoretical contact angles equal to 90°, whereas experimental results [13] indicated that such a transition takes place at contact angles smaller than 90°. In the past we derived for radial grooves a more general equation $\cos\theta_r = D_r(1-D_f)\cos\theta - D_f$ [14]. Taking into account periodic circular grooves [6] and including a Gaussian average over roughness amplitudes, we studied the contact angle of Al droplets on Al_2O_3 (reactive wetting). Because a rough surface can be considered as a combination of circular and radial grooves [14], a measure of the experimental contact angle is the inverse rms value (θ_{rg}) defined as: $1/\theta_{rg}^2 = (1/2)(1/\theta_g^2 + 1/\theta_r^2)$. Indeed the transition angle was found to be lower than 90° [14] in agreement with experimental observations.

Despite the insights of the influence of roughness on wetting achieved by periodic groove models, up to now a quantitative treatment of the influence of random roughness at a submicron length scale on apparent contact angles is missing. This will be the topic of the present work. Surface roughness will be described by an rms amplitude Δ, an in-plane roughness correlation length ξ (average distance between consecutive hills or valleys on the surface), and a roughness exponent H (degree of surface irregularity at short length scales, i.e. for the range smaller than ξ). The morphology described by these three parameters is termed as a self-affine fractal [15, 16], and it is known to occur in a wide variety of physical systems (e.g., vapour deposited metal films under nonequilibrium conditions, fractured surfaces etc.) [17, 18]. Moreover, it provides a rather general concept to describe randomness, that can be modeled rather efficiently.

2. CONTACT ANGLE MODELS

In this section we will reformulate the equations of the periodic groove (geometrical) [1–6] and thermodynamic [10] models that have been used to estimate apparent contact angles.

2.1. Geometrical model

Following the model of periodical grooves presented in earlier studies [1–6], the contact angle of a liquid that partially wets a random rough surface (with respect to the average flat surface) will be given by the theoretical contact angle θ (described by Young's equation) which is modified by the angle of the local slope at the surface, namely $\theta_g = \theta + \tan^{-1}(|\vec{\nabla} h|)$. For a weak roughness ($|\vec{\nabla} h| \ll 1$; $\tan^{-1}|\vec{\nabla} h| \cong |\vec{\nabla} h|$ [19]) and ensemble averaging over possible roughness configurations, we obtain to first order $\langle\theta_g\rangle \cong \theta + \langle|\vec{\nabla} h|\rangle$. Assuming a Gaussian height–height distribution [20–22] with a root–mean–square roughness $\langle|w|^2\rangle^{1/2}$ and an average roughness, i.e. an arithmetic average of the height, the identity $\langle|w|\rangle = [(2/\pi)\langle|w|^2\rangle]^{1/2}$ holds. The maximum contact angle is given by

$$\langle\theta_g\rangle \cong \theta + (2/\pi)^{1/2}\rho, \quad (1)$$

where $\rho = [\langle|\vec{\nabla} h|^2\rangle]^{1/2}$ and ρ is the rms of the local slope. Substituting in $\rho = [\langle|\vec{\nabla} h|^2\rangle]^{1/2}$ the Fourier transform of the surface height $h(\vec{q}) = (2\pi)^{-2}\int h(\vec{r})e^{-i\vec{q}\cdot\vec{r}}d^2\vec{r}$ with $\vec{r} = (x,y)$ the in-plane position vector and assuming $\langle h(\vec{q})h(\vec{q}\,')\rangle = [(2\pi)^4/A]\delta^2(\vec{q}-\vec{q}\,')\langle|h(\vec{q})|^2\rangle$, i.e. translation invariance, the rms local slope ρ is given by

$$\rho = \{[(2\pi)^2/A]\int_{0<q<Q_c} q^2\langle|h(\vec{q})|^2\rangle d^2\vec{q}\}^{1/2} \quad (2)$$

with A the average flat surface area, $A \approx \int d^2\vec{r}$ and $Q_c = \pi/a_o$ an upper cut-off with a_o to the order of the atomic spacing [23].

2.2. Thermodynamic model

Following Wensel's approach, i.e. assuming that the liquid wets the crevices at the surface upon contact [10],† the contact angle is given by

† Such an assumption is reasonable for weak roughness surfaces ($H \geq 0.5$ and $\Delta/\xi \ll 1$) which are considered in the present study.

$\theta_w = \cos^{-1}\{D_r \cos\theta\}$ with $D_r = A_r/A$. $A_r = \int \sqrt{1 + |\vec{\nabla} h|^2} d^2\vec{r}$ represents the rough surface area. For a weak roughness of $|\vec{\nabla} h| \ll 1$ and ensemble averaging over roughness configurations, we obtain up to second order $\langle A_r \rangle \cong A + (1/2)\int \langle |\vec{\nabla} h|^2 \rangle d^2\vec{r} - (3/8)\int \langle |\vec{\nabla} h|^4 \rangle d^2\vec{r}$. Substituting the Fourier transform of $h(\vec{r})$ and assuming translation invariant surfaces (see also Appendix A), the contact angle is found to be:

$$\langle \theta_w \rangle \cong \cos^{-1}\{[1 + (1/2)\rho - (3/8)\rho^2]\cos\theta\}. \quad (3)$$

Equation (3) can be obtained, because for Gaussian random variables the ensemble average of an odd product of h is zero, while that of an even product equals the sum of the variables grouped in pairs of two in all possible ways (see also Appendix A) [20–22]. Further the actual calculation of the contact angles using equations (1–3) requires knowledge of the roughness spectrum $\langle |h(\vec{q})|^2 \rangle$.

3. SELF-AFFINE ROUGHNESS MODEL

A wide variety of real surfaces/interfaces are well described by a roughness associated with a self-affine fractal scaling [15] in terms of fractional Brownian motion [16–18]. Actually, the function of Brownian motion, i.e. a single valued function of variable t in which the increments possess a Gaussian distribution, is transformed to a description of a surface profile as a random process. The introduction of statistical methods to surface profilometry was originally due to Abbott and Firestone [24]. The bearing area curve for a surface profile specification was in fact the cumulative probability function for surface height, i.e. the conventional statistical approach for the representation of random events. The Gaussian distribution and its application was put on a firm footing by Greenwood *et al*. [25]. They argue that surfaces are formed by many independent effects and the overall result is subject to a cumulative effect that is governed by the Gaussian form. For self-affine fractals the roughness spectrum $\langle |h(\vec{q})|^2 \rangle$ scales as [16–18]

$$\langle |h(\vec{q})|^2 \rangle \propto \begin{cases} q^{-2-2H} \text{ if } q\xi \gg 1 \\ \text{const if } q\xi \ll 1 \end{cases} \quad (4)$$

where the roughness exponent H is a measure of the degree of surface irregularity [26], such that smaller values of H characterize more jagged or irregular surfaces at short roughness wavelengths ($<\xi$). The scaling behavior of equation (4) is satisfied by the simple Lorentzian model [27, 28],† $\langle |h(\vec{q})|^2 \rangle = [A/(2\pi)^5][\Delta^2\xi^2/(1 + aq^2\xi^2)^{1+H}]$ with $a = (1/2H)[1-(1 + aQ_c^2\xi^2)^{-H}]$ if $0<H<1$, and $a = (1/2)\ln[1 + aQ_c^2\xi^2]$ if $H = 0$. The latter model yields an analytic expression of the rms local slope ρ (equation (2)) [23]

$$\rho = (\Delta/\xi)(a\sqrt{2})^{-1}\{(1-H)^{-1}[(1 + aQ_c^2\xi^2)^{1-H} - 1] + H^{-1}[(1 + aQ_c^2\xi^2)^{-H} - 1]\}^{1/2} \quad (5)$$

simplifying the contact angle calculations in terms of equations (1) and (3).

4. RESULTS–DISCUSSION

For $H>0$ and $Q_c\xi \gg 1 (\xi \gg a_o)$, equation (5) yields $\rho \approx \Delta/\xi^H$ which implies that the maximum geometrical contact angle (equation (1)) varies as $\langle \theta_g \rangle \approx \theta + (2/\pi)^{1/2}(\Delta/\xi^H)$. The latter is for $H = 1$ comparable with the prediction from the periodical groove model [3–5], i.e. $\theta_g \cong \theta + \sqrt{2/\pi}(\Delta/\xi)$ if wetting proceeds perpendicular to the grooves. In the opposite extreme case $H = 0$ (logarithmic roughness) equation (5) yields the local slope $\rho \approx (\pi/\sqrt{2a}>(\Delta/a_o)$ for $Q_c\xi \gg 1$ or alternatively a contact angle of $\langle \theta_g \rangle \approx \theta + (\pi/a)^{1/2}(\Delta/a_o)$.

Our calculations were performed for self-affine roughness, which has been observed in a wide variety of surfaces of thin films [16–18]. As was shown in earlier studies the rms local slope ρ depends strongly on the roughness exponent H and the long wavelength roughness ratio Δ/ξ [23]. Figure 1 depicts the contact

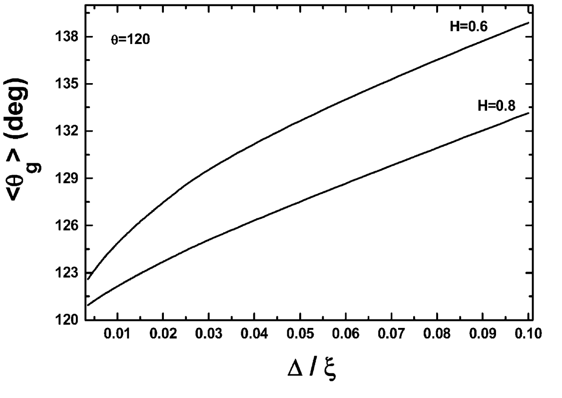

Fig. 1. Calculation of the effect of roughness on the contact angle $\langle \theta_g \rangle$ as a function of the long wavelength ratio Δ/ξ for two almost consecutive roughness exponents H, $a_o = 0.3$ nm, and $\Delta = 1$ nm.

† Besides the simplicity of $\langle |h(q)|^2 \rangle$, its Fourier transform yields the analytically solvable correlation function $C(r) = [\Delta^2/a\Gamma(1 + H)]r/2a^{1/2}\xi)^H K_H(r/2a^{1/2}\xi)$ with $Kv(x)$ the second kind Bessel function of order v.

angle $<\theta_g>$, that is related to the rms local slope, as a function of Δ/ξ over one order of magnitude for various roughness exponent. For $\Delta/\xi \ll 1$ with smoothing effects at long wavelengths the contact angle approaches asymptotically to the theoretical value θ predicted by Young's equation.

In the thermodynamic approach of equation (3), the substrate roughness has the opposite effect on the apparent contact angle for theoretical angles θ below or above 90° as is shown in Fig. 2. At increasing roughness at short and/or long wavelengths ($H \sim 1$ and/or $\Delta/\xi \ll 1$) the apparent contact angle $<\theta_w>$ decreases below 90°, while above this value it increases with increasing roughness. However, the influence of roughness diminishes as θ approaches 90° (Fig. 2). In Fig. 3(a) the influence of a variation of the roughness parameters is displayed. It depicts the dependence of $<\theta_w>$ on the ratio Δ/ξ, whereas in Fig. 3(b) the dependence of $<\theta_w>$ on the roughness exponent H for $\Delta/\xi \ll 1$ is shown. A comparison reveals that the effect of H on the contact angle is rather distinct with respect to that of the roughness ratio Δ/ξ.

In many cases of partial wetting an absorbed ultrathin liquid (or precursor) film is formed [1–5], with the liquid drop lying on that film rather than on the bare substrate surface. Thus, at short wavelengths the effective surface will be smoothened by a surface tension with as the lower cut-off length scale the healing length ζ. For van der Waals interactions ζ scales with the (precursor) film thickness d as $\zeta \propto d^2$ [3–5, 29, 30]. Thus, for a precursor film that is molecularly thin, i.e. implying also short healing lengths $\ll \xi$, and at sufficient large roughness correlation lengths ($\xi \gg \zeta$), we may ignore the smoothing effect of the healing length. In any other case such a smoothing effect can be taken effectively into account by replacing the atomic roughness cut-off Q_c in equation (5) by $Q_\zeta = \pi/\zeta$. It leads to a smaller surface slopes ρ and consequently to a weaker roughness effect on the apparent contact angle.

Because rough surfaces can be considered as a combination of radial and circular grooves, it is reasonable to consider an rms value of $<\theta_g>$ and $<\theta_w>$ of the form $[(1/2)\{<\theta_w>^2 + <\theta_g>^2\}]^{1/2}$ [14]. However, the apparent contact angle $<\theta_g>$ overestimates the effect of roughness, because in this case the maximum rms local surface slope is considered. In order to reduce the contribution of $<\theta_g>$ and taking into account the fact that $<\theta_w><<\theta_g>$, the reciprocal rms contact angle $<\theta_{gw}>$ defined by [14]

$$\frac{2}{<\theta_{gw}>^2} = \frac{1}{<\theta_w>^2} + \frac{1}{<\theta_g>^2} \qquad (6)$$

can be used to minimize properly the large contribution of $<\theta_g>$ as was suggested also in former reactive wetting studies [14]. The average contact angle $<\theta_{gw}>$ defined by equation (6) lies in between the angles $<\theta_w>$ and $<\theta_g>$ ($<\theta_w> \le <\theta_{gw}> \le <\theta_g>$) because $<\theta_w><<\theta_g>$.

Figure 4 shows the rms contact angle $<\theta_{gw}>$ which display a similar behaviour of what is observed by Wenzel's equation (Fig. 2). However, the transition angle θ_{tr} is shifted to values below 90° which is in agreement with periodic groove model predictions [14]. The precise value of the shift depends on

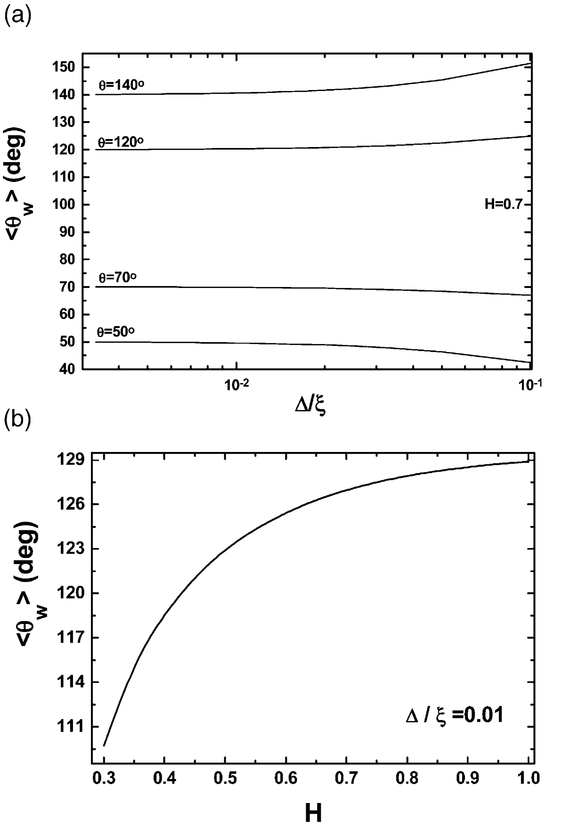

Fig. 3. (a) Calculation of the effect of roughness on the contact angle $<\theta_w>$ vs. Δ/ξ for a theoretical contact angle θ, $a_o = 0.3$ nm, $\Delta = 1$ nm. (b) $<\theta_w>$ vs the roughness exponent H for the same theoretical contact angle θ, and $\Delta/\xi = 0.01$.

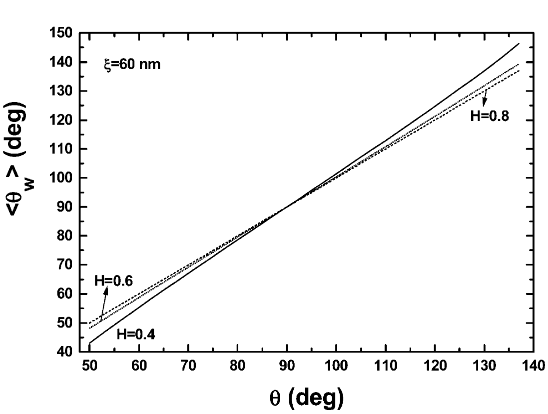

Fig. 2. Calculation of the effect of roughness on the contact angle $<\theta_w>$ vs. theoretical values θ for $a_o = 0.3$ nm, $\Delta = 1$ nm.

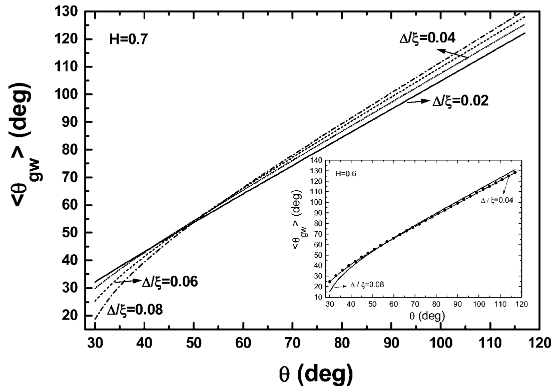

Fig. 4. Calculation of the rms contact angle $<\theta_{gw}>$ vs. the theoretical values of θ for $H = 0.7$, $a_o = 0.3$ nm, $\Delta = 1$ nm. The transition angle θ_{tr} is lower than 90°. The inset displays similar plots for slightly different roughness exponent $H = 0.6$ to show the sensitivity of θ_{tr} on H.

the particular roughness parameters. In particular the roughness exponent H influences the transition angle considerably in such a way that as H increases θ_{tr} decreases rather rapidly. Indeed, as the inset of Fig. 4 indicates, a small change of H may alter the transition angle by more than 10° (for $H = 0.7$ we have $\theta_{tr} \approx 50°$, while for $H = 0.6$: $\theta_{tr} \approx 60°$).

Figure 5(a) depicts the variation of the normalized apparent contact angle $<\theta_{gw}>/\theta$ as a function of the long wavelength ratio Δ/ξ. For theoretical contact angles θ lower than 90°, a weak maximum is observed at a rather small ratio of Δ/ξ (~0.02). For larger roughness ratios, $<\theta_{gw}>/\theta$ is an decreasing function of Δ/ξ for contact angles θ lower than θ_{tr}, while $<\theta_{gw}>/\theta$ increases with increasing ratio Δ/ξ for $\theta > \theta_{tr}$. A comparison reveals that the influence of the roughness ratio Δ/ξ is more pronounced in the regime of theoretical contact angles $\theta < \theta_{tr}$. Figure 5(b) shows the influence of the roughness exponent H which affects slightly the position of the maximum in such a way that as H increases it occurs at a larger ratio of Δ/ξ. However, in the regime of a physically relevant ratio Δ/ξ (~0.1), as the roughness exponent H increases the decrement of $<\theta_{gw}>/\theta$ weakens rather significantly and it reflects the drastic influence of H on the rms local surface slope ρ [23].

Our results will be qualitatively valid for other self-affine fractal roughness models [31–33] describing the roughness spectrum $<|h(\vec{q})|^2>$ which is restricted to obey the asymptotic scaling limits as defined by equation (4). This is so because the rms local surface slope scales in any case as $\rho \propto \Delta/\xi^H (\xi \gg a_o)$ apart from some multiplying factors inherent to the specific model.

5. CONCLUSIONS

It is shown that the apparent contact angle depends critically on the roughness exponent H and on the long wavelength ratio Δ/ξ. The particular behavior

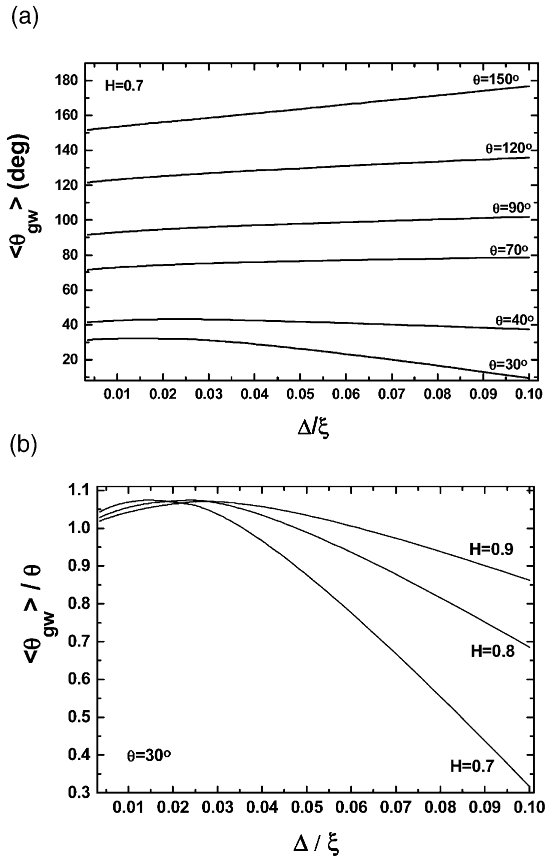

Fig. 5. (a) Influence of the ratio Δ/ξ on the normalized contact angle $<\theta_{gw}>/\theta$ for $H = 0.7$, $a_o = 0.3$ nm, $\Delta = 1$ nm. A maximum is observed at low Δ/ξ (~0.02), while for large Δ/ξ the behavior $<\theta_{gw}>/\theta$ is altered for theoretical contact angles above and below the transition angle $\theta_{tr}(<90°)$. (b) $<\theta_{gw}>/\theta$ vs. Δ/ξ, for $\theta(=30°) < \theta_{tr}$, for various values of H.

depends on the value of the theoretical contact angle θ determined by Young's equation with respect to the transition angle θ_{tr}.

Our calculations were performed in the weak roughness limit ($\rho \ll 1$) in order to minimize effects due to partial wetting of rough grooves. It is also called the composite case [1–5]. Moreover, our findings compare qualitatively with former studies based on periodically grooved rough surfaces [13, 14]. Smoothing effects due to the existence of a precursor film which can be significant for a roughness with a short correlation length $\xi \sim \zeta$) will led to weaker roughness effects yielding qualitatively similar results. Finally, future work will be necessary to address also the issue of the composite case (unwetted sharp surface grooves) which is expected to takes place in the strong roughness limit ($\rho > 1$).

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APPENDIX A

The assumption of $h(r)$ being a Gaussian variable means that the average of any odd number of factors of $h(r)$ with the same or different arguments vanishes, whereas the average of the product of an even number of factors of $h(r)$ is given by the sum of the products of the averages of $h(r)$'s paired two-by-two in all possible ways, i.e., we have [34]

$$\begin{aligned} <h(r)h((r')h(r'')h(r''')> &= <h(r)h(r')> \\ &<h(r'')h(r''')> + <h(r)h(r'')> \\ &<h(r')h(r''')> + <h(r)h(r''')> \\ &<h(r')h(r'')> \end{aligned} \tag{A1}$$

Fourier transformation of equation (A1) yields

$$\begin{aligned} &<h(q)h(q')h(q'')h(q''')> \\ &= <h(q)h(q')><h(q'')h(q''')) \\ &+ <h(q)h(q'')><h(q')h(q''')> \\ &+ <h(q)h(q''')><h(q')h(q'')> \end{aligned} \tag{A2}$$

where each pair in equation (A2) can be calculated according to:

$$i^{2n}\int <\prod_{j=1}^{2n} h(q_j)> \prod_{j=1}^{2n} q_j e^{-i(\sum_{j=1}^{2n} q_j)r} \prod_{j=1}^{2n} d^2q_j = P(n)\rho^{2n} \tag{A3}$$

will appear with $i^{2n} = (-1)^n$. Thus, the integrals in equation (A3) for $n = 1,2$ will be given by

$$\begin{aligned} &-\int \\ &<h(q_1)h(q_2)>(q_1 \cdot q_2)e^{-i(q_1 + q_2)r}d^2q_1d^2q_2 \\ &= <(\nabla h)^2> = \rho^2 \end{aligned} \tag{A4}$$

$$\int <\prod_{j=1}^{4} h(q_j)>(\prod_{j=1}^{4} q_j)e^{-i(\sum_{j=1}^{4} q_j)r} \prod_{j=1}^{4} d^2q_j = 3<(\nabla h)^4> = 3\rho^4 \tag{A5}$$

For higher order terms further concepts of statistics are needed to calculate $P(n)$ which represents all possible ways to group $2n-h(q)$'s ensemble averaged in pairs of two [20–22].