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Published in:
Physical Review. B: Condensed Matter and Materials Physics

DOI:
[10.1103/PhysRevB.68.035412](https://doi.org/10.1103/PhysRevB.68.035412)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2003

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):
Palasantzas, G., & Backx, GMEA. (2003). Wetting of van der Waals solid films on self-affine rough surfaces. *Physical Review. B: Condensed Matter and Materials Physics*, 68(3), [035412].
<https://doi.org/10.1103/PhysRevB.68.035412>

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Wetting of van der Waals solid films on self-affine rough surfaces

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(Received 5 November 2002; revised manuscript received 7 March 2003; published 16 July 2003)

In this work we investigate the influence of random self-affine substrate roughness on the solid layer thickness under conditions of triple-point wetting of adsorbed van der Waals films. Our calculations show that a significant solid film thickness λ_s can be reached (in the nanometer range) for substrate roughness parameters $w/\xi \leq 0.05$ and/or $H \approx 1$ with w the rms roughness amplitude, ξ the lateral roughness correlation length, and H the roughness exponent ($0 \leq H \leq 1$). Independent of substrate-particle and particle-particle interactions, with increasing roughness exponent H and/or decreasing ratio w/ξ the solid film thickness λ_s increases since the substrate surface becomes smoother. Finally, the solid layer thickness is shown to be sensitive to growth details of the substrate roughness as described in many cases in terms of dynamic scaling theory.

DOI: 10.1103/PhysRevB.68.035412

PACS number(s): 68.08.Bc, 64.70.Hz, 68.35.Rh

Wetting phenomena of solid substrates constitute a topic of intense research from both the fundamental^{1,2} and technological³⁻⁵ points of view. Wetting of liquids on flat solid substrates is well understood from the microscopic point of view,^{1,2,6} and it is driven by the strong substrate-particle (van der Waals) attraction forces. In this case, the liquid film thickness is described as a function of substrate-particle and particle-particle interactions for specified thermodynamic parameters (pressure P and temperature T). Experiments with noble gases¹ on different substrates confirmed that the thickness of the wetting layer increases with increasing substrate-particle attraction (for fixed parameters P and T). Complete wetting occurs for stronger substrate-particle attraction than particle-particle interactions, and approaching liquid-gas coexistence for system temperature T higher than the triple point temperature T_3 . For $T < T_3$ a solid film of finite thickness λ_s is formed close to the sublimation line. Indeed, the solid film thickness λ_s is always finite when solid-gas coexistence is approached.⁷⁻¹¹ This case is called complete solid wetting in contrast to liquids where during complete wetting the thickness becomes infinite.⁷⁻¹³

There is a major difference between solid and liquid wetting due to the inability of a solid film to relax the elastic compression originating by the substrate attraction, which is incorporated by the reduced substrate-particle Hamaker constant R . This is incorporated in the Gittes-Schick (GS) theory¹¹ for solid film adsorption on flat substrates. Complete solid wetting occurs for $R = R_o$ (λ_s is still finite), while for $R > R_o$ the solid film thickness λ_s decreases with increasing R .¹¹ However, the GS theory applies only to flat substrates. Recently, it was shown that the key parameter governing adsorption of solid films is the substrate roughness, rather than the elastic deformation caused by the particle-substrate attraction.¹² Moreover, it was shown by theory and confirmed by experiment that a finite substrate roughness leads to triple-point wetting, and reduces the solid layer thickness λ_s .¹² Analytic calculations of the roughness factor were given for the case of self-affine rough surfaces, which were

described by the roughness exponent H , the rms roughness amplitude w , and the in-plane roughness correlation length ξ .¹³ Indeed, for a wide variety surfaces, i.e., the nanometer scale topology of vapor deposited thin films, eroded and fractured surfaces etc., the associated roughness morphology is well quantified in terms of self-affine scaling.^{14,15} At any rate, precise characterization of substrate roughness is necessary in solid layer wetting situations i.e., in coatings of sculpted substrates, curved nanoparticles,^{16,17} etc.

In this work we will show quantitatively the effect of the substrate roughness parameters w , ξ , and H on the solid layer thickness λ_s by taking also into account specific elastic properties of the wetting solid layer film, and the strength of the substrate-particle and particle-particle interactions. Indeed, in the previous work¹³ it was shown only qualitatively the effect of the parameters w , ξ , and H by ignoring contributions arising from the free energy penalty due to the substrate attraction and assuming pressures solely at gas/solid coexistence.

For rough solid substrates, the wetting layer thickness (for fixed T and P) is obtained by minimization of the excess grand canonical free energy (per unit area) $\Sigma(\lambda_s, \ell_\ell) = \Sigma_1(\lambda_s, \ell_\ell) + \Sigma_2(\lambda_s) + \Sigma_3(\lambda_s)$.^{11,12} It is assumed that a liquid film of thickness ℓ_ℓ is on top of a solid film, which is on top of the rough solid substrate. $\Sigma_1(\lambda_s, \ell_\ell)$ is the thermodynamic part,^{1,18} $\Sigma_2(\lambda_s)$ the free energy penalty due to substrate attraction,^{7,11} and $\Sigma_3(\lambda_s)$ the elastic free energy due to solid layer bending caused by substrate roughness. Thus, we have briefly^{11,12,19,20}

$$\Sigma_1 = \gamma_{ws} + \gamma_{s\ell} + \gamma_{\ell g} - \gamma_{wg} + \lambda_s(P_o - P) \frac{\rho_s}{\rho_g} + \ell_\ell(P'_o - P) \frac{\rho_\ell}{\rho_g} + \frac{A_1}{\lambda_s^2} + \frac{A_2}{\ell_\ell^2} + \frac{A_3}{(\lambda_s + \ell_\ell)^2}, \quad (1)$$

$$\Sigma_2 = -\frac{3E}{2(1+\nu)} S^2 (\lambda_s^{-1} + S \lambda_s^{-2}), \quad (2)$$

$$\Sigma_3 = \frac{E\lambda_s^3}{24(1-\nu^2)} \frac{1}{A} \int_A \{(\nabla^2 h)^2 + 2(1-\nu)[(\partial_{xy}^2 h)^2 - \partial_{xx}^2 h \partial_{yy}^2 h]\} d^2 \vec{r}, \quad (3)$$

with γ 's the extrapolated interfacial tension between wall (w), solid (s), liquid (ℓ), and gas (g). E is the Young's modulus of the solid film and ν its poisson ratio. P_o and P'_o are the coexistence pressures respectively between gas/solid and gas/liquid. ρ_g , ρ_ℓ , and ρ_s are the number densities at gas/solid and gas/liquid coexistence ($\rho_g \ll \rho_\ell < \rho_s$). C and H_c are respectively the Hamaker constants for the substrate/particle and particle/particle interaction potentials with $A_1 = (\rho_s - \rho_\ell)(C - \rho_s H_c)$, $A_2 = (\rho_s - \rho_\ell)\rho_\ell H_c$, and $A_3 = \rho_\ell(C - \rho_s H_c)$.¹ $S = 0.0229(R - R_o)\sigma$ with $R = C/H_c\rho_s$ and σ a molecular length.¹¹

The substrate roughness is described by a single valued random function $h(\vec{r})$ of the in-plane position vector $\vec{r}$ ($\langle h(\vec{r}) \rangle = 0$) with A the average flat macroscopic area. Far away from the triple point at the solid-gas coexistence ($\ell_\ell = 0$), the equilibrium solid thickness λ_s is obtained by minimisation of $\Sigma(\lambda_s, \ell_\ell)$ or $\partial \Sigma(\lambda_s, \ell_\ell) / \partial \lambda_s|_{\ell_\ell=0} = 0$ which yields¹³

$$\frac{\rho_s}{\rho_g}(P_o - P) - 2 \frac{(C - \rho_s H_c)}{\lambda_s^3} \rho_s + \frac{3E}{2(1+\nu)} \frac{S^2}{\lambda_s^2} \left(1 + \frac{2S}{\lambda_s}\right) + \frac{\partial \Sigma_3}{\partial \lambda_s} = 0. \quad (4)$$

If we define the Fourier transform $h(\vec{r}) = \int h(\vec{q}) e^{-i\vec{q} \cdot \vec{r}} d^2 \vec{q}$ we obtain,¹³ $\partial \Sigma_3 / \partial \lambda_s = [E\lambda_s^2 / 8(1-\nu^2)] \times [(2\pi)^4 / A] \int_{0 \leq |\vec{q}| < Q_c} q^4 \langle |h(\vec{q})|^2 \rangle d^2 \vec{q}$ (for translation invariant roughness), $\langle \dots \rangle$ an ensemble average over possible roughness configurations, and $\langle |h(\vec{q})|^2 \rangle$ the roughness spectrum. $Q_c = \pi/c_o$ is an upper roughness cut-off with c_o of the order of atomic dimensions. For self-affine fractal roughness $\langle |h(\vec{q})|^2 \rangle$ scales as a power law $\langle |h(\vec{q})|^2 \rangle \propto q^{-2-2H}$ if $q\xi \gg 1$, and $\langle |h(\vec{q})|^2 \rangle \propto \text{const}$ if $q\xi \ll 1$.^{14,15} The roughness exponent H is a measure of the degree of surface irregularity.^{14,15,21} This scaling behavior is satisfied²¹ by the roughness spectrum $\langle |h(\vec{q})|^2 \rangle = [A/(2\pi)^5] [w^2 \xi^2 / (1 + aq^2 \xi^2)^{1+H}]$ with $a = (1/2H)[1 - (1 + aQ_c^2 \xi^2)^{-H}]$ for $0 < H < 1$.

Our calculations were performed for roughness amplitude $w = 5$ nm, $c_o = 0.3$ nm, $\nu = 0.3$, and $\sigma = 0.3$ nm, Hamaker constants $H_c = 2.44 \times 10^{-6}$ eV nm⁶ and $C = 0.39 \times 10^{-3}$ eV nm³,¹² $R_o = 1.88$,¹² and density ratio $\rho_s/\rho_g = 700$. The parameters H_c , C , and R_o correspond to solid hydrogen.¹² Grain boundaries in the solid layer are neglected, while local defect formation in the solid near the substrate interface can be included since they will only alter the γ 's.²² Moreover, the present theory requires weak roughness so that $|\nabla h| < 1$ or quantitatively $\rho_{rms} = \sqrt{\langle |\nabla h|^2 \rangle} < 1$.¹³

Figure 1 shows the evolution of the solid layer thickness λ_s (for $P = P_o$) as a function of the substrate in-plane roughness correlation length ξ . As the surface becomes smoother at large length scales, which corresponds to a decreasing ratio w/ξ , the solid layer thickness clearly increases. The increment of λ_s is faster and larger in magnitude for lower values

FIG. 1. Solid layer thickness λ_s (for $P = P_o$) as a function of the substrate in-plane roughness correlation length ξ for large roughness exponent $H = 0.9$.

of the elastic modulus E which correspond to lower attraction induced strain energy and lower bending energy due to substrate roughness.

The effect of the roughness exponent H becomes more pronounced if we consider the variation of the solid layer thickness λ_s as a function of the ratio R (particle-substrate to particle-particle interactions) as can be seen in Fig. 2. As a function of R the solid thickness has a maximum at $R = R_o$ (complete solid wetting) and further decreases for $R > R_o$ in agreement with the general scenario of the GS theory. The effect of the roughness exponent H is more pronounced for interaction ratios around the maximum at $R = R_o$ ($S = 0$) where complete solid wetting occurs (λ_s is always finite when solid-gas coexistence is approached^{7-10,11}). Moreover, the magnitude of λ_s decreases faster for smoother surfaces at short length scales or larger roughness exponents H as Fig. 2 indicates.

The observed maximum of the solid layer thickness λ_s around $R \approx R_o$ becomes more pronounced for large roughness exponents $H \approx 1$ as Fig. 2 indicates, and lower values of the elastic modulus E as is shown in Fig. 3. Furthermore, as Fig. 4 shows, the solid layer thickness λ_s increases rather fast in magnitude with decreasing long wavelength rough-

FIG. 2. Solid layer thickness λ_s (for $P = P_o$) as a function of the reduced stress ratio R/R_o for $E = 1$ Pa, $\xi = 500$ nm ($w/\xi = 0.01$), and two different exponents H . The dotted line indicates $R = R_o$.

FIG. 3. Solid layer thickness λ_s (for $P=P_o$) as a function of the reduced stress ratio R/R_o with $H=0.9$, $\xi=500$ nm (ratio $w/\xi=0.01$), and various values of E . The dotted line indicates $R=R_o$.

ness ratio w/ξ when the pressure P is close to the pressure P_o for gas/solid coexistence. Similar is the situation if we consider the variation of the solid layer thickness λ_s for two slightly different roughness exponents H as Fig. 5 shows. Clearly, the effect of the roughness exponent H is more pronounced for smoother surfaces or smaller ratios w/ξ . In any case, the modulation of the solid layer thickness λ_s by changing the substrate roughness is clearly more effective for thermodynamic conditions close to solid/gas coexistence.

Our calculations can be used for wetting studies on self-affine rough substrates formed by non-equilibrium deposition of metal solid films (i.e., Au, Ag, Cu, etc.).^{14,15} Self-affine roughness can be formed by deposition of metal films onto Si-oxide surfaces or other substrates at relatively low temperatures (i.e., close to room temperature).^{14,15,23} Variation of deposition parameters (deposition rate, substrate temperature, film thickness) can alter the solid thin film (substrate) roughness parameters,^{14,15} which in turn can be used as an alternative way to control tripple point wetting phenomena.

Therefore, one might consider to modulate substrate roughness by depositing a metal film with various thickness, which effectively yields different roughness parameters w , ξ ,

FIG. 4. Solid layer thickness λ_s as a function of the ratio w/ξ for $R=4.5$, $H=0.9$, $E=100$ Pa and various values of the pressure ratio P/P_o .

FIG. 5. Solid layer thickness λ_s as a function of the ratio w/ξ for $R=4.5$, two consecutive roughness exponents H , $E=100$ Pa and $P/P_o=0.5(<1)$.

and H . A wide variety of growth dynamic studies in the past have shown that the roughness parameters w and ξ can evolve with film thickness (for constant deposition rate) as power-laws such that $w \propto h^b$ and $\xi \propto h^c$, while the exponent H remains independent from thickness changes.^{14,15} If $c=b/H$ then the local surface slope is an invariant of the problem (or $\rho_{rms}=\text{const}$) which also yields an invariant roughness contribution to λ_s as is shown in Fig. 6 (dotted line). In our calculations we have taken the growth exponent $b=0.25$ smaller than 1 so that $w < d$ with $w=(d/10)^b$ (nm), the roughness exponent $H=0.8$, and dynamic exponents c in the range $c \geq b/H$ with $\xi=10(d/10)^c$ (nm).^{14,15} The solid layer thickness λ_s shows significant sensitivity on the dynamic exponent c when $c > b/H$. This is because as the correlation length ξ increases much faster than the rms roughness amplitude w significant smoothing occurs, leading to lower roughness contribution since $\Sigma_3 \sim w^2/\xi^4$.¹³

In conclusion, we explored quantitatively the influence of the roughness parameters w , ξ , and H that characterize random self-affine substrate roughness on the solid layer thickness λ_s of adsorbed van der Waals films. It shown that a significant film thickness λ_s (in the nanometer range) can be achieved for substrate roughness parameters $w/\xi < 0.01$ and $H > 0.5$. Indeed, nanometer thickness (≥ 10 nm) van der

FIG. 6. Solid layer thickness λ_s (for $P=P_o$) as a function of the substrate film thickness d for $R=4.5$, roughness exponent $H=0.8$, and $E=100$ Pa.

Waals film are necessary in diverse research areas, which include neutrino rest mass determination,²⁴ laser fusion,²⁵ slow muon surface investigations,²⁶ and optical spectroscopy.²⁷ Finally, the solid layer thickness is shown to be sensitive to substrate roughness growth details, which are described in many cases in terms of scaling exponents that

determine the thickness evolution of the roughness parameters w and ξ .

We would like to acknowledge support from the “Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO).”

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