Wetting of van der Waals solid films on self-affine rough surfaces
Palasantzas, Georgios; Backx, GMEA

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

DOI:
10.1103/PhysRevB.68.035412

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

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):

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.
Wetting phenomena of solid substrates constitute a topic of intense research from both the fundamental and technological points of view. Wetting of liquids on flat solid substrates is well understood from the microscopic point of view, 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 gases 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 \(\lambda_s\) is formed close to the sublimation line. Indeed, the solid film thickness \(\lambda_s\) is always finite when liquid-gas coexistence is approached.

This case is called complete solid wetting in contrast to liquids where during complete wetting the thickness becomes infinite.

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) theory for solid film adsorption on flat substrates. Complete solid wetting occurs for \(R = R_o\) (\(\lambda_s\) is still finite), while for \(R > R_o\), the solid film thickness \(\lambda_s\) decreases with increasing \(R\), with the GS theory applying 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.

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 \(\lambda_s\). 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 \(\xi\). Indeed, for a variety of 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.

At any rate, precise characterization of substrate roughness is necessary in solid layer wetting situations i.e., in coatings of sculpted substrates, curved nanoparticles, etc.

In this work we will show quantitatively the effect of the substrate roughness parameters \(w, \xi, H\) on the solid layer thickness \(\lambda_s\) 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 work it was shown only qualitatively the effect of the parameters \(w, \xi, H\) 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 (fixed \(T\) and \(P\)) is determined by minimization of the excess grand canonical free energy (per unit area) \(\Sigma(\lambda_s, \xi, H)\), which is the thermodynamic part, \(\Sigma_1(\lambda_s, \xi, H)\), the free energy penalty due to substrate attraction, \(\Sigma_2(\lambda_s)\), and \(\Sigma_3(\lambda_s)\), the elastic free energy due to solid layer bending caused by substrate roughness. Thus, we have

\[
\Sigma = \Sigma_1 + \Sigma_2 + \Sigma_3
\]

where

\[
\Sigma_1 = \gamma_{gs} + \gamma_{rt} + \gamma_{lg} - \gamma_{rg} + \lambda_s (P_o - P) \frac{\rho_A}{\rho_s} + \xi (P'_o - P) \frac{\rho_A}{\rho_s}
\]

\[
\Sigma_2 = -\frac{3E}{2(1+\nu)} S^{2} (\lambda^{-1}_s + S\lambda^{-2}_s)
\]

\[
\Sigma_3 = \frac{A_1}{\lambda^2_s} + \frac{A_2}{\xi^2} + \frac{A_3}{(\lambda_s + \xi)^2}
\]

and \(S\) is the rms roughness amplitude.
\[
\sum_3 = \frac{E\lambda_s^3}{24(1-\nu^2)} \frac{1}{A} \int_A [\nabla^2 h]^2 + 2(1-\nu)[(\partial_{xy}^2 h)^2 - \partial_x^2 h \partial_y^2 h)] d^2 \vec{r},
\]

with \(\gamma\) 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 \(\nu\) its poison ratio. \(P_0\) and \(P_0'\) are the coexistence pressures respectively between gas/solid and gas/liquid. \(\rho_s\), \(\rho_L\), and \(\rho_g\) are the number densities at gas/solid and gas/liquid coexistence (\(\rho_g < \rho_L < \rho_s\)). \(C\) and \(H_c\) are respectively the Hamaker constants for the substrate/particle and particle/particle interaction potentials with \(A_1 = (\rho_s - \rho_g)(C - \rho_c H_c)\), \(A_2 = (\rho_g - \rho_L)\rho_c H_c\), and \(A_3 = \rho_c (C - \rho_s H_c)\). \(\frac{S}{2} = 0.0229(R - R_o)\sigma\) with \(R = C/H_c \rho_s\) and \(\sigma\) a molecular length.\(^{11}\)

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

\[
\frac{\rho_s}{\rho_g} \left( P_0 - P \right) - 2 \frac{(C - \rho_c H_c)}{\lambda_s^3} + \frac{3E}{2(1+\nu)} \frac{S^2}{\lambda_s^3} \left[ 1 + \frac{2S}{S_{\lambda_s}} \right] \frac{d^2 \vec{r}}{2} = 0.
\]

If we define the Fourier transform \(h(\vec{q}) = (\hat{h}(\vec{q}))e^{-i\vec{q}\cdot\vec{r}}d^2 \vec{q}\) we obtain,\(^{13}\)

\[
\partial \Sigma / \partial \lambda_s = [E\lambda_s^3/(1-\nu^2)] \times [(2\pi)^4 / A] \int_{0<|\vec{q}|<Q_c} d^2 \vec{q} \frac{\langle |\hat{h}(\vec{q})|^2 \rangle}{\langle |\hat{h}(\vec{q})|^2 \rangle} \langle |\hat{h}(\vec{q})|^2 \rangle \frac{d^2 \vec{q}}{2} = 0
\]

for translation invariant roughness, \(\langle \cdot \rangle\) an ensemble average over possible roughness configurations, and \(\langle |\hat{h}(\vec{q})|^2 \rangle\) the roughness spectrum. \(Q_c = \pi \ell_c / c_o\) is an upper roughness cut-off with \(c_o\) of the order of atomic dimensions. For self-affine fractal roughness \(\langle |\hat{h}(\vec{q})|^2 \rangle\) scales as a power law \(\langle |\hat{h}(\vec{q})|^2 \rangle \approx q^{-2-2H}\) if \(q \ell_c \gg 1\), and \(\langle |\hat{h}(\vec{q})|^2 \rangle \approx \text{const} \) if \(q \ell_c \ll 1\).\(^{14,15}\) The roughness exponent \(H\) is a measure of the degree of surface irregularity.\(^{14,15,21}\) This scaling behavior is satisfied\(^{21}\) by the roughness spectrum \(\langle |\hat{h}(\vec{q})|^2 \rangle = [A/(2\pi)^3] [\hat{W}(\xi^2)^{3/2}] (1 + a q^2 \xi^2)^{1+H}\) with \(a = (1/2H)[1 - (1 + a q^2 \xi^2)^{-H}]\) 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 nm\(^6\) and \(C = 0.39 \times 10^{-3}\) eV nm\(^3\);\(^{12}\) \(R_o = 1.88,^{12}\) and density ratio \(\rho_s / \rho_L = 700\). 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 \(\gamma\)’s.\(^{22}\) Moreover, the present theory requires weak roughness so that \(\int |\nabla h|^2 < 1\) or quantitatively \(\rho_{\text{rms}} = (\int |\nabla h|^2) < 1.13\)

Figure 1 shows the evolution of the solid layer thickness \(\lambda_s\) (for \(P = P_0\)) as a function of the substrate in-plane roughness correlation length \(\xi\). As the surface becomes smoother at large length scales, which corresponds to a decreasing ratio \(w/\xi\), the solid layer thickness clearly increases. The increment of \(\lambda_s\) is faster and larger in magnitude for lower values 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 \(\lambda_s\) 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 (\(\lambda_s\) is always finite when solid-gas coexistence is approached\(^{3-10,11}\)). Moreover, the magnitude of \(\lambda_s\) 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 \(\lambda_s\) 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 \(\lambda_s\) increases rather fast in magnitude with decreasing long wavelength roughness correlation length \(\xi\).
ness ratio $w/\xi$ 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 $\lambda_s$ 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 $w/\xi$. In any case, the modulation of the solid layer thickness $\lambda_s$ 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.). 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). Variation of deposition parameters (deposition rate, substrate temperature, film thickness) can alter the solid thin film (substrate) roughness parameters, which in turn can be used as an alternative way to control triple 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 $w$, $\xi$, and $H$. A wide variety of growth dynamic studies in the past have shown that the roughness parameters $w$ and $\xi$ 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. 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 $\lambda_s$ 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 $c = b/H$ with $\xi = 10(d/10)^c$ (nm). The solid layer thickness $\lambda_s$ shows significant sensitivity on the dynamic exponent $c$ when $c > b/H$. This is because as the correlation length $\xi$ increases much faster than the rms roughness amplitude $w$ significant smoothening occurs, leading to lower roughness contribution since $\Sigma \lambda_s \sim w^2/\xi^4$.

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

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

*Corresponding author. Email address: g.palasantas@phys.rug.nl