

The structure of the water-propane interface investigated by x-ray reflectivity measurements

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We present an x-ray reflectivity study of the propane-water interface. The vertical structure of the interface is analyzed and the adsorption of thin layers of propane on the water surface is observed. An increase of layer thickness with rising pressure is found. The electron density of the thin films is identical with the corresponding value of bulk liquid propane. From the adsorption isotherm we determine the Hamaker constant of the system which shows a considerable higher value compared to calculations based on the Lifshitz theory. The surface tension of the molecularly thin layer is reduced in comparison to the bulk value. The measured surface roughness is in good agreement with a modified model based on capillary wave fluctuations of the water-propane-gas interfaces.

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I. INTRODUCTION

Several techniques are used to measure adsorption isotherms of gases on surfaces [1–9]. Most commonly volumetric or gravimetric methods are used to determine the loss of gas volume or the increase of the sample weight during the exposure to a gas atmosphere. These techniques require samples with large surfaces such as porous materials. The layer thickness can be calculated by the knowledge of the adsorbing area. However, details of the vertical structure of the adsorbed films and their surfaces are not accessible. A direct access to the thickness of the adsorbed layer enables the surface plasmon spectroscopy [2, 3] with a sub-nanometer resolution of the layer thickness. Because of the restriction of this method to metallic substrates only adsorption on solid surfaces can be measured with this technique. Similar resolution in layer thickness can be achieved by ellipsometry measurements [6–8]. Only the demand of sharp interfaces restricts this method to systems where the surface roughness is small in comparison with the layers thickness.

In this work, adsorption experiments of the water-propane interface are presented. It is shown that an x-ray reflectivity setup can be used to determine adsorption isotherms, resolving the vertical structure of liquid gas interface with high resolution. The film thickness of adsorbed thin films as well as the surface roughnesses are determined. Based on this information the coupling between layer and substrate and the surface tension of the molecularly thin film can be derived. Thus, the validity of Lifshitz theory based formalism for calculation of coupling constants [10] can be investigated for molecularly thin films.

The adsorption of alkane molecules on water surfaces was investigated by previous studies. Methods such as the capillary rise technique [11] or the drop-shape method [12] lead to a determination of the surface tension of water as a function of temperature, pressure and the gas used in the experiment but gave no information about the surface structure of the adsorbed layer. A decrease of the water surface tension with rising gas pressure was observed. Gas chromatography was used by Karger *et al.* to investigate liquid-gas-systems [4, 5]. The discussion of this experimental data which also does not supply any structural information about the film and its surface can be found in [13–16]. Ragil *et al.* [7] and Bertrand *et al.* [8] used ellipsometry measurements to investigate pentane and propane-hexane mixture films on water surfaces. Wetting transition between thin films (below 100 Å) and thick films are reported and interpreted in a change of the coupling constant which describes the film-substrate interaction.

Thus, in contrast to the above mentioned indirect methods for the determination of adsorption isotherms, in this work the first direct analysis with Angström resolution of molecularly thin adsorbed films on a water surface is presented.

The relative low condensation pressure of propane $p_0 = 4.74$ bar at $T = 0^\circ\text{C}$ allows to record a complete adsorption isotherm using a conventional x-ray source. The solubility of propane in water is around 10^{-5} [17]. Thus the system water-propane can be described as nearly non soluble. This leads to a sharp interface between the water and the adsorbed propane phase which is affected by capillary wave fluctuations. Therefore, the water-propane interface serves as an ideal system to study adsorption of thin films on liquids surfaces.

The paper is structured as follows: in the next section the x-ray reflectivity technique is presented. Section 3 describes the experimental setup. Section four comprises the data analysis and the discussion of the results. The paper is completed by a short summary and conclusions.

II. THEORY OF X-RAY REFLECTIVITY

The technique of x-ray reflectivity provides information about the electron density profile perpendicular to the surface. The wave vector transfer has only one component which is given by $q_z = (4\pi/\lambda) \sin \alpha$, where λ denotes the wavelength of the radiation and α the angle between the surface and the x-ray beam. A general description of the x-ray reflectivity technique is given in [18–23]. Assuming a simple model consisting of two rough interfaces, i.e. a substrate-layer interface and a layer-gas interface, the three dimensional electron density profile can be described as a sum of two Heaviside-functions H

$$\rho(x, y, z) = \Delta\rho_1 H(z - z_1(x, y)) + \Delta\rho_2 H(z - z_2(x, y)), \quad (1)$$

where $\Delta\rho_1$ denotes the electron density contrast between the substrate and the layer and $\Delta\rho_2$ is the electron density contrast between the layer and the gas. The coordinate z describes the direction perpendicular, while x and y are the directions parallel to the surface. The vertical positions of the substrate-layer interface and the layer-gas interface are determined by $z_1(x, y)$ and $z_2(x, y)$. With this model the scattered intensity at the specular condition can be calculated via the first Born approximation [18]

$$I(q_z) \propto \frac{1}{q_z^4} \left((\Delta\rho_1)^2 e^{-q_z^2 \sigma_{1\text{eff}}^2} + (\Delta\rho_2)^2 e^{-q_z^2 \sigma_{2\text{eff}}^2} + 2\Delta\rho_1 \Delta\rho_2 \cos(q_z l) e^{-q_z^2 \frac{\sigma_{1\text{eff}}^2 + \sigma_{2\text{eff}}^2}{2}} \right) \quad (2)$$

with the layer thickness l , and the effective surface roughnesses $\sigma_{1\text{eff}}$ and $\sigma_{2\text{eff}}$ of the interfaces. The surface roughness $\sigma_{i\text{eff}}$ ($i = 1, 2$) is defined by $\sigma_{i\text{eff}} = \frac{A}{4\pi^2} \int_{q_{\text{res}}}^{q_{\text{uc}}} d\mathbf{q} < \tilde{z}_i(\mathbf{q}) \tilde{z}_i(-\mathbf{q}) >$ where $\tilde{z}_i(\mathbf{q})$ denotes the Fourier transform of $z_i(\mathbf{r})$ and A is a unit area. For a liquid surface decorated by capillary waves the upper wave vector cutoff q_{uc} is given by the inverse of the size r_m of the molecules $q_{\text{uc}} = \pi/r_m$. The lower wave vector cutoff q_{res} is given by the experimental resolution. This value is determined by the resolution of the diffractometer via $q_{\text{lc}} = q_z \Delta\alpha/2$, where $\Delta\alpha$ is the measured angular acceptance of the detector [19, 20]. The third term in Eq. (2) causes the appearance of Kiessig fringes in a reflectivity scan. The oscillation period Δq_z is directly connected to the layer thickness via $l = 2\pi/\Delta q_z$. The electron density contrast and the roughness of the interfaces can be determined by using Eq.(2) in a fitting procedure of the data. Usually the electron density is expressed as dispersion δ which is related to the electron density ρ_e of the sample via $\delta = r_e \rho_e \lambda^2 / (2\pi)$ where r_e is the classical electron radius.

III. EXPERIMENT

The development of a pressure cell for x-ray reflectivity experiments enables a direct observation of adsorption processes on liquid surfaces by determining the electron density profile of the adsorbed material as a function of gas pressure. The demand of transparency of the sample cell for x-rays in combination with temperature, pressure and mechanical stability renders experiments difficult.

The x-ray measurements were performed with a Bruker D8-Advanced diffractometer in theta-theta geometry. The x-ray radiation is produced by an x-ray tube with copper anode and focused by a Goebel mirror yielding a parallel x-ray beam of wavelength $\lambda = 1.54 \text{ \AA}$. For the detection of the scattered radiation a NaI scintillation detector was used. The x-ray beam height was 0.1 mm with a width of 10 mm. The resulting angular resolution was approximately $\Delta\alpha = 0.4 \text{ mrad}$.

The sample cell was built in order to measure x-ray reflectivities with high temperature and high pressure stability. Its design is based on a sample cell described in [24], with two chambers, of which the outer cell can be evacuated or pressurized up to 2 bar. The inner cell can be pressurized up to approximately 5 bar. The liquid sample is placed on a stainless steel plate with a diameter of 120 mm and a depth of 2 mm. Two thermal sensors (Pt100 elements) monitor the temperature of the gas and of the liquid. The inner cell is mounted on a heat exchanger, which stabilizes the sample temperature with an accuracy of 20 mK via a Lakeshore control unit. The pressure is monitored by a pressure gauge with a resolution of 1 mbar. The stability was 20 mbar during a typical reflectivity scan. Both, the inner and outer cell have 50 μm thick Kapton windows for the incoming and reflected x-ray beam. Water from a millipore system and propane 3.5 (C_3H_8) from Messer Griessheim was used. All reflectivity measurements were performed at a water temperature of 0°C. After filling the water into the sample container the inner cell was filled with a nitrogen gas atmosphere of 1 bar and cooled down to 0°C. Then an x-ray reflectivity of the bare nitrogen-water interface was measured. Before taking reflectivities of the propane water interface the inner cell was flushed for several minutes

with gaseous propane. After this, x-ray-reflectivities were measured at different pressures between 1.0 bar and 4.6 bar, which is close to the saturation pressure of propane at a temperature of 0°C, ($p_0=4.74$ bar [25]). At higher gas pressures the outer cell was pressurized with N₂ up to 2 bar to relieve the Kapton windows of the inner cell. For background subtraction of the diffusely scattered intensity, each reflectivity scan was followed by a longitudinal diffuse scan with an angular detector offset of 0.1°. One reflectivity scan took approximately 3 hours and was repeated several times (excepted the 4.6 bar measurement) in order to check the data for reproducibility.

IV. DATA ANALYSIS AND DISCUSSION

Reflectivity scans of the propane water interface are shown in Fig. (1) for pressures between 1.0 bar and 4.6 bar. The oscillation in the reflectivity recorded at higher pressures is due to the formation of a thin layer on the water surface.

Because of strong absorption of the gas atmosphere and the limited intensity of a x-ray tube compared to a synchrotron source the reflectivity could be reached up to a maximum wave vector of $q_z = 0.45 \text{ \AA}^{-1}$. In the first step of the data analysis the measured diffuse background was subtracted for all reflectivity scans. Then each reflectivity scan was refined using the effective density model [18]. For the bare water surface a roughness of $\sigma_{\text{water}} = (3.65 \pm 0.3) \text{ \AA}$ was obtained. Calculation of substrate roughness for systems consisting of two components with high surface tension difference show that the substrates roughness is not significantly affected by the overlaying film [31]. Thus, σ_{water} was set constant for all other measurements. The water dispersion was found to be $\delta_{\text{water}} = 3.7 \cdot 10^{-6}$ for all measurements, which is due to the low solubility of propane in water. Results of all refinements are also presented in Figure 1. The difference between refinement and measured data at a pressure of 4.6 bar is due to a temporary temperature instability which occurs in the q_z range between 0.07 and 0.11 \AA^{-1} . Because of the short relaxation times which are needed to reach the equilibrium state this reflectivity was refined excluding the mentioned q_z region. All refined layer thickness and roughness for the measurements are summarized in table I.

The reflectivities can be refined by assuming a simple model of one adsorbed layer of liquid propane on the water surface. Figure 2 shows the dispersion profiles of the water-propane system normalized to the value of the water dispersion. The dispersion of bulk liquid propane $\delta_{\text{prop}} = 1.9 \cdot 10^{-6}$ is marked by a horizontal dashed line in figure 2.

The increase of the layer thickness from 3.4 \AA to 25 \AA with increasing gas pressure can be described by an adsorption isotherm within the framework of the FHH (Frenkel-Halsey-Hill) [26–29] theory. The layer thickness dependent part of interfacial potential for the substrate and the adsorbed layer of thickness l at gas pressure p per unit area is given by

$$\Delta G = -\frac{A_{\text{eff}}}{12\pi l^2} + l\Delta\rho k_{\text{B}}T \log(p_0/p), \quad (3)$$

where p_0 denotes the saturation pressure of the gas, and $\Delta\rho$ the particle density difference between the adsorbed liquid and its vapor phase. The temperature and pressure dependent densities of the liquid and gaseous phase of propane are accessible via reference [25]. The interaction between the substrate and the film is described by an effective Hamaker constant A_{eff} . k_{B} is the Boltzmann constant. A stable film requires the interfacial potential to be minimized, which results in an equilibrium film thickness l_{m} or the so-called adsorption isotherm

$$l_{\text{m}} = \left(\frac{A_{\text{eff}}}{6\pi\Delta\rho k_{\text{B}}T \log(p/p_0)} \right)^{1/3}. \quad (4)$$

As shown in [30, 31] the layer thickness l_{m} is increased by capillary wave fluctuations which leads to an effective layer thickness l_{mg} given by

$$l_{\text{mg}} = l_{\text{m}} + 2\frac{\sigma_{\text{h}}^2}{l_{\text{m}}}, \quad (5)$$

where σ_{h} is the surface roughness in the framework of the harmonic approximation (see below) [30, 31].

The thicknesses of the adsorbed propane layers as a function of the relative pressure p/p_0 are presented in Figure 3. The refinement with Eq. 5 (solid line in figure 3) leads to an effective Hamaker constant of $A_{\text{eff}} = -1.2 \cdot 10^{-19} \text{ J}$, which is a surprisingly high value. The effective Hamaker constant can be estimated using the Lifshitz theory [10]:

$$\begin{aligned}
A_{\text{eff,th}} \approx & \frac{3}{4} k_B T \left(\frac{\epsilon_{\text{sub}} - \epsilon_{\text{lay}}}{\epsilon_{\text{sub}} + \epsilon_{\text{lay}}} \right) \left(\frac{\epsilon_{\text{gas}} - \epsilon_{\text{lay}}}{\epsilon_{\text{gas}} + \epsilon_{\text{lay}}} \right) \\
& + h\nu_e \frac{3}{8\sqrt{2}} \frac{(n_{\text{sub}}^2 - n_{\text{lay}}^2)}{\sqrt{n_{\text{sub}}^2 + n_{\text{lay}}^2} \sqrt{n_{\text{gas}}^2 + n_{\text{lay}}^2}} \\
& \cdot \frac{(n_{\text{gas}}^2 - n_{\text{lay}}^2)}{\left(\sqrt{n_{\text{sub}}^2 + n_{\text{lay}}^2} + \sqrt{n_{\text{gas}}^2 + n_{\text{lay}}^2} \right)}.
\end{aligned} \tag{6}$$

$n_{\text{sub,lay,gas}}$ are the index of refraction of the substrate, layer and gas at a wavelength of 589 nm and $\epsilon_{\text{sub,lay,gas}}$ the accompanying static dielectric constants, $\nu_e \approx 3 \cdot 10^{15}$ Hz [10]. For the system water - liquid propane - gaseous propane all parameters necessary to calculate A_{eff} are summarized in table 1.

The calculation of the effective Hamaker constant using Eq. 6 yields to $A_{\text{eff,th}} = -2 \cdot 10^{-22}$ J. The calculated adsorption isotherm given by Eq. 5, using the theoretical effective Hamaker constant is also shown in figure 3 as a dashed line for comparison.

The large discrepancy between the calculated and the measured value of the Hamaker constant shows that eq.(5) seems not to be correct for molecularly thin liquid films. The meanfield based description of the system by the index of refraction and the static dielectric constant measured for a wavelength of 589 nm are assumed to be valid over all length scales. This assumption seems to be justified for the water and the gas phases but not for the thin adsorbed layer which thickness is close to atomic length scales. Moreover, the roughness of the adsorbed layer may play an important role. A closer examination especially of the frequency dependent part of the Hamaker constant shows that the effective Hamaker constant is strongly effected by n_{lay} . Figure 4 shows this behavior. The effective Hamaker constant is calculated using equation 6 as a function of n_{lay} . $A_{\text{eff,th}}$ shows a strong variation around the literature value marked by a the vertical line. A reduction of the index of refraction shifts the effective Hamaker constant by approximately 2 orders of magnitude but does not resolve the discrepancy between the experiment and the theory completely. An additional variation of the static dielectric constant does not change the effective Hamaker constant drastically and can therefore not account for the discrepancy. The large Hamaker constant seems to be a characteristic of molecular thin films, since thicker films are well described by theoretical treatment using Hamaker constants given by equation 6 [7, 8].

The experiment shows an increase of the surface roughness from $\sigma = 3.1 \text{ \AA}$ to $\sigma = 8.0 \text{ \AA}$ with increasing film thickness. This thickness dependent surface roughness of the film can be explained by the van der Waals interaction between the liquid water substrate and the propane layer which affects the capillary wave induced surface roughness of the liquid layer [18, 23]. The thickness dependent capillary wave roughness of the adsorbed layer can be calculated using a theory described in [31] which is based on a Taylor expansion of the interfacial potential. Depending on the layers thickness the Taylor expansion can be stopped after the second order term (high film thickness) leading to the surface roughness σ_{h} in the framework of the harmonic approximation. For low film thicknesses the expansion has to be proceeded to the forth order term leading to the surface roughness σ_{ah} (anharmonic approximation). Following this calculation the capillary wave induced surface roughness of a very thin adsorbed liquid film is

$$\begin{aligned}
\sigma_{\text{ah}}^2 = & \frac{k_B T}{4\pi\gamma_2} \ln \left(\frac{B/\gamma_2 + q_{\text{uc}}^2}{B/\gamma_2} \right) \\
& \times \left(1 - D \frac{k_B T}{4\pi} \left(\frac{1}{\gamma_2 B} - \frac{1}{\gamma_2 B + q_{\text{uc}}^2} \right) \right),
\end{aligned} \tag{7}$$

where γ_2 is the surface tension of the film. $B = (\partial^2 \Delta G / \partial l^2)|_{l_m}$ and $D = (\partial^4 \Delta G / \partial l^4)|_{l_m}$ denote the coupling parameters arising from the water-propane interaction. In the framework of this theory the surface roughness of the substrate is not influenced by the adsorbed film if a high difference in surface tension between substrate and film exists. Figure 5 shows the refined surface roughness of the propane layer as a function of the layer thickness. The dashed line represents the calculation of the surface roughness σ_{ah} according to Eq.7 with a surface tension for the liquid propane layer from Ref. [25] ($\gamma_2=10.1$ mN/m) and the effective Hamaker constant of $-1.2 \cdot 10^{-19}$ J. It becomes clear that the experimental data is not well described especially for large layer thicknesses. The best fit of the data (solid line) results in a value of $\gamma_2=3.8$ mN/m which is considerably smaller than the surface tension of bulk liquid propane. This observation, however, is not unique to the water-propane system as lower surface tensions of thin liquid films have been observed also for thin alkane wetting films on silicon substrates [32], for liquid hydrogen on a gold substrate [33], and for thin isobutane films on glycerol [31].

V. SUMMARY AND CONCLUSION

In summary, x-ray reflectivity measurements were performed in order to investigate the structure of the water-propane interface. The adsorption of molecularly thin liquid films consisting of propane molecules on the water surface was observed. The observed layer thickness as a function of the reduced pressure can be well described by a FHH adsorption isotherm. The interaction between the water substrate and the adsorbed layer, which is given by the effective Hamaker constant was determined. The value found for the Hamaker constant of the propane-water system is considerable larger than expected from theory. The Lifshitz theory based approach for the calculation of the effective Hamaker constant cannot explain the measured Hamaker constant for molecularly thin films. A wetting transition between two different wetting states such as reported for mixtures of alkanes on water [8] was not observed. The surface roughnesses of the adsorbed films was determined and a reduction of the surface tension of the adsorbed layers of approximately 1/3 when compared to bulk liquid propane was observed. This finding appears to be an intrinsic feature of molecularly thin films. Taking this into account the measured surface roughness is in good agreement with a model based on capillary waves fluctuations of a liquid thin film in an external potential [31].

VI. ACKNOWLEDGEMENT

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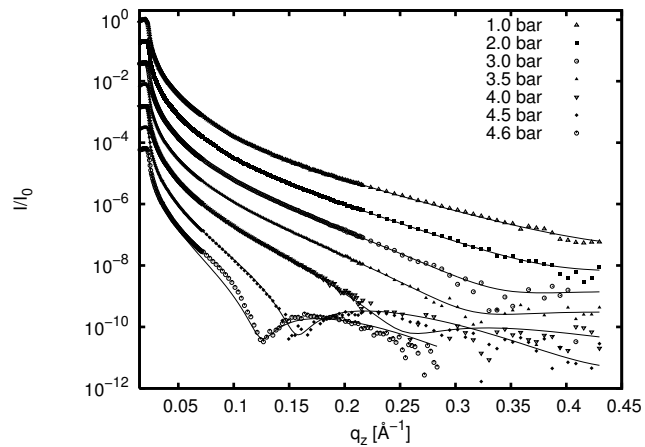


FIG. 1: X-ray reflectivities of the water-propane interface at different propane pressures between 1.0 and 4.6 bar. The solid lines display the refinements of the data using the effective density model. The difference between refinement and measured data at a pressure of 4.6 bar is due to a temporary temperature instability.

TABLE I: Refined layer thickness and roughness for all measurements.

pressure $p \pm 0.02$ [bar]	layer roughness $\sigma \pm 0.5$ [Å]	layer thickness $l_m \pm 1.00$ [Å]
1.00	3.1	3.4
2.00	3.7	5.9
3.00	3.9	8.1
3.50	4.5	9.0
4.00	5.5	12.0
4.50	6.0	20.0
4.60	7.7	25.0

TABLE II: The parameters for the calculation of the effective Hamaker constant. a: see Ref. [25], b: extrapolation from data of butane, pentane, hexane and octane from Ref. [17].

	substrate	layer	gas
ϵ	80.1 ^a	1.6678 ^b	1.0020 ^a
n	1.3343 ^a	1.3387 ^a	≈ 1

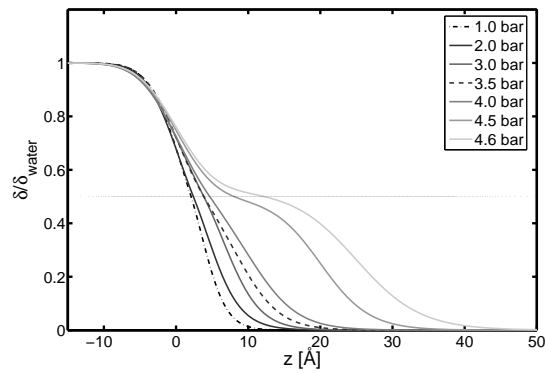


FIG. 2: Dispersion profiles of the water-propane interface obtained by the refinement of the reflectivities assuming a single layer model. The dispersion is normalized to the bulk water dispersion. The horizontal dotted line marks the dispersion of liquid propane.

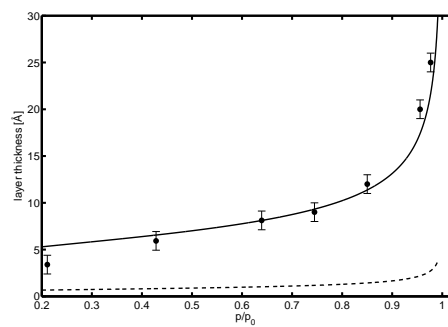


FIG. 3: Adsorption isotherm of propane on a water surface as deduced from the X-ray data. The pressure is normalized to the saturation pressure of propane $p_0 = 4.7$ bar at $T=0^\circ\text{C}$. The solid line represents the FHH isotherm with an effective Hamaker constant of $-1.2 \cdot 10^{-19}$ J. The dashed line shows the calculated isotherm using an effective Hamaker constant of $-2.5 \cdot 10^{-22}$ J as obtained from Eq. 5

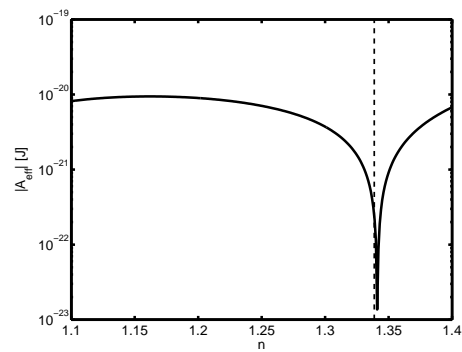


FIG. 4: The effective Hamaker constant calculated for the water propane system using eq.6 as a function of the refractive index of the layer n_{lay}

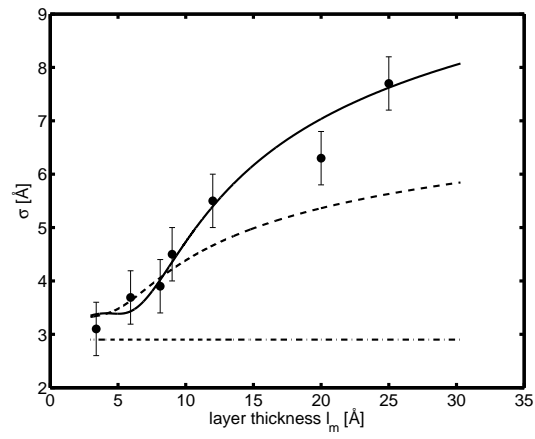


FIG. 5: Surface roughness of molecularly thin propane films on a water surface as function of the layer thickness. Solid line: calculated surface roughness using eq. 7 and a surface tension of $\gamma_2 = 3.8$ mN/m. Dashed line: $\gamma_2 = 10$ mN/m. The point-dashed line represents the roughness of the water surface.