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An ellipsometric study of the surface freezing of liquid alkanes

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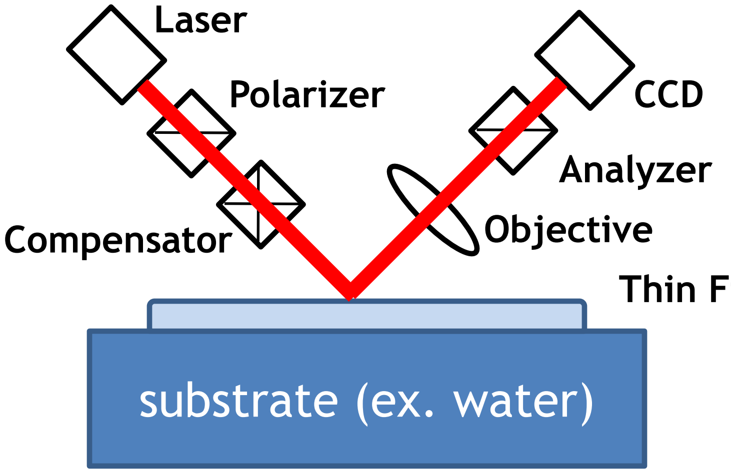
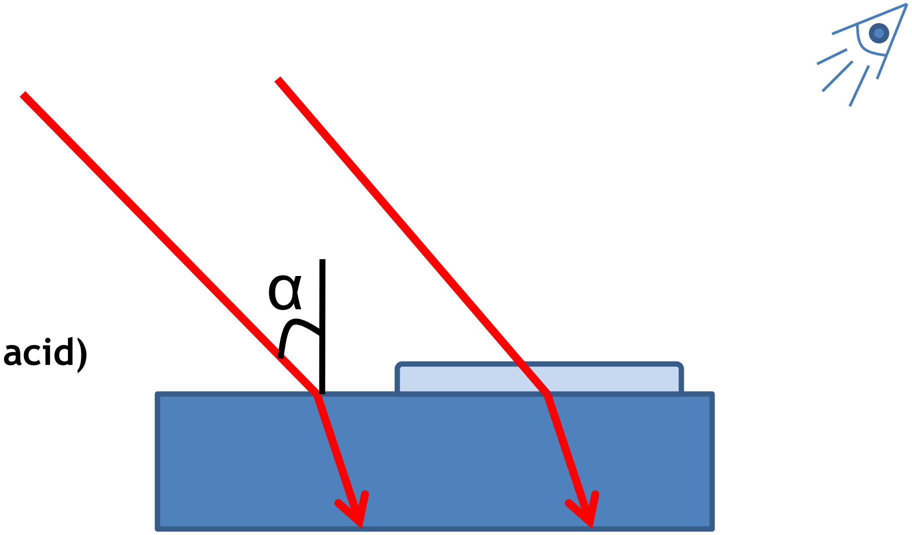
Introduction – ellipsometry at thin films

Imaging Ellipsometry (IE) VS **NULL Ellipsometry (in that paper)**





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Δ, ψ: ellipsometric angle obtained

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We can obtained by Re(r) + Im(r)

Brewster's Law
tan $\alpha = n_2/n_1$

Using the Brewster's law only obtained by Im(r)

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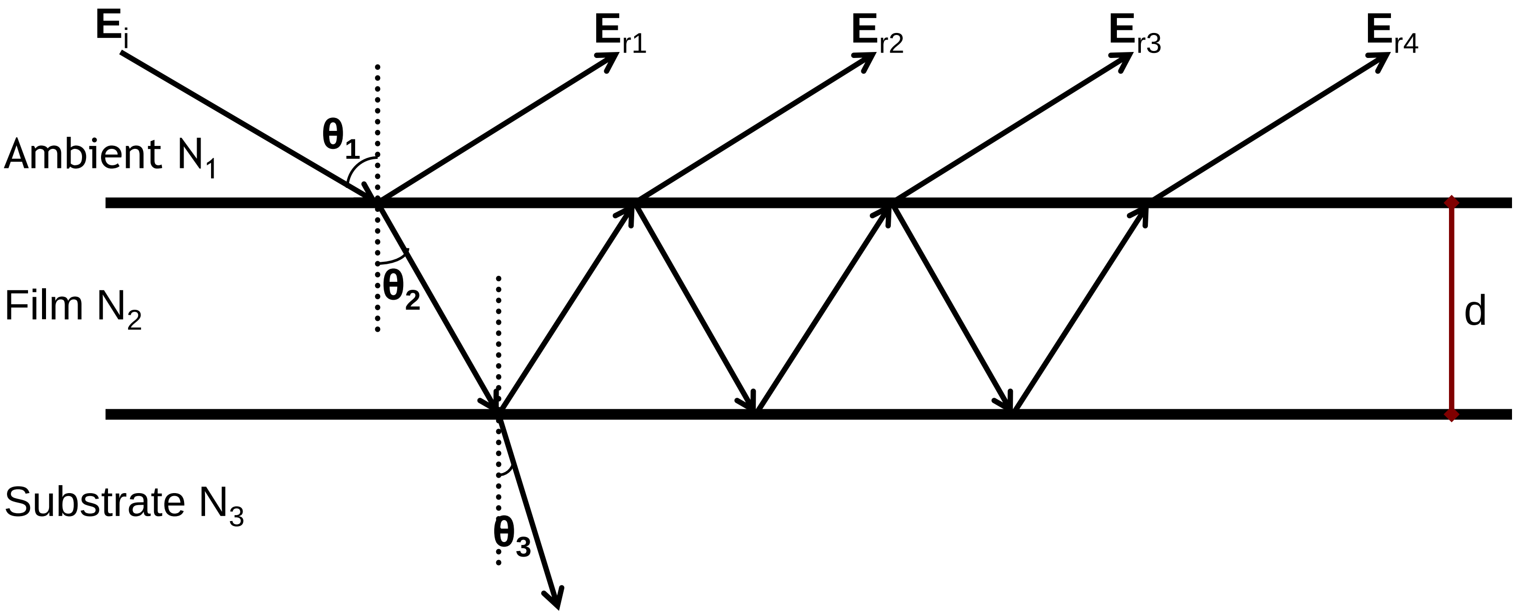
Principles of Ellipsometry

Fig. 1 Film-Covered Surface



Phase Difference : $\beta = 2\pi(\frac{d}{\lambda})N_2 \cos\theta_2$

Total Reflective Coefficient :

$$r = r_{12} + t_{12}t_{21}r_{23}e^{-i2\beta} + t_{12}t_{21}r_{21}r_{23}^2e^{-i4\beta} + t_{12}t_{21}r_{21}^2r_{23}^3e^{-i6\beta} + \cdots$$

Principles of Ellipsometry

$$r = r_{12} + t_{12}t_{21}r_{23}e^{-i2\beta}\left\{1+(r_{21}r_{23}e^{-i2\beta})+(r_{21}r_{23}e^{-i2\beta})^2+(r_{21}r_{23}e^{-i2\beta})^3+\cdots\right\}$$

The sum of the geometric series :

$$r = r_{12} + \frac{t_{12}t_{21}r_{23}e^{-i2\beta}}{1-r_{21}r_{23}e^{-i2\beta}}$$

In Fresnel’s Identities

$$r_{21} = -r_{21}$$

$$t_{21} = \frac{1-r_{12}^2}{t_{12}}$$

Fresnel equation

$$r_p = \frac{E_{rp}}{E_{ip}} = \frac{N_2\cos\theta_1 - N_1\cos\theta_2}{N_2\cos\theta_1 + N_1\cos\theta_2}$$

$$r_s = \frac{E_{rs}}{E_{is}} = \frac{N_1\cos\theta_1 - N_2\cos\theta_2}{N_1\cos\theta_1 + N_2\cos\theta_2}$$

$$t_p = \frac{2N_1\cos\theta_1}{N_2\cos\theta_1 + N_1\cos\theta_2}$$

$$t_s = \frac{2N_1\cos\theta_1}{N_1\cos\theta_1 + N_2\cos\theta_2}$$

Principles of Ellipsometry

$$r = \frac{r_{12} + r_{23} e^{-i2\beta}}{1 + r_{12} r_{23} e^{-i2\beta}}$$

Similarly….

$$t = -\frac{t_{12} t_{23} e^{-i2\beta}}{1 + r_{12} r_{23} e^{-i2\beta}}$$

Ellipsometry Parameters: Δ, Ψ

$$r_p \equiv \frac{E_{rp}}{E_{ip}} = \left| r_p \right| e^{i\delta_p} \qquad r_s \equiv \frac{E_{rs}}{E_{is}} = \left| r_s \right| e^{i\delta_s}$$

IN THAT PAPER (measured by Im(r) part)

Im(r) at Re(r) = 0

$$\rho = \frac{r_p}{r_s} = \left| \frac{r_p}{r_s} \right| e^{i(\delta_p - \delta_s)} \equiv \tan \Psi e^{i\Delta} = \mathrm{Re}(r) + \mathrm{Im}(r)$$

Principles of Ellipsometry – inhomogeneous dielectric surface

Im(r)=$\bar{\rho}$ at Re(r)=0 $d/\lambda \gg 1$

At perfect interface

$$\eta = \frac{\lambda}{\pi} \frac{(\epsilon_1 - \epsilon_2)}{\sqrt{\epsilon_1 + \epsilon_2}} \bar{\rho}. \qquad (1)$$

η_r Surface roughness

η_d Surface density variation → η Can originate from three contributions

η_a Surface anisotropy

The value of η depends upon the particular profile, different profiles can have the same value.

Principles of Ellipsometry – inhomogeneous dielectric surface

$$\eta = \eta_r + \eta_d + \eta_a$$

Fermi profile

$$\begin{aligned}\eta &= \eta_{\mathrm{r}} + \eta_{\mathrm{d}} + \eta_{\mathrm{a}} \\ &= \frac{t}{4.394}(\epsilon_1 - \epsilon_2)\ln\left(\frac{\epsilon_2}{\epsilon_1}\right) \\ &\quad + \int \mathrm{d}z \frac{[\epsilon_z(z) - \epsilon_1][\epsilon_z(z) - \epsilon_2]}{\epsilon_z(z)} \\ &\quad + \int \mathrm{d}z[\epsilon_x(z) - \epsilon_z(z)]. \end{aligned} \tag{2}$$

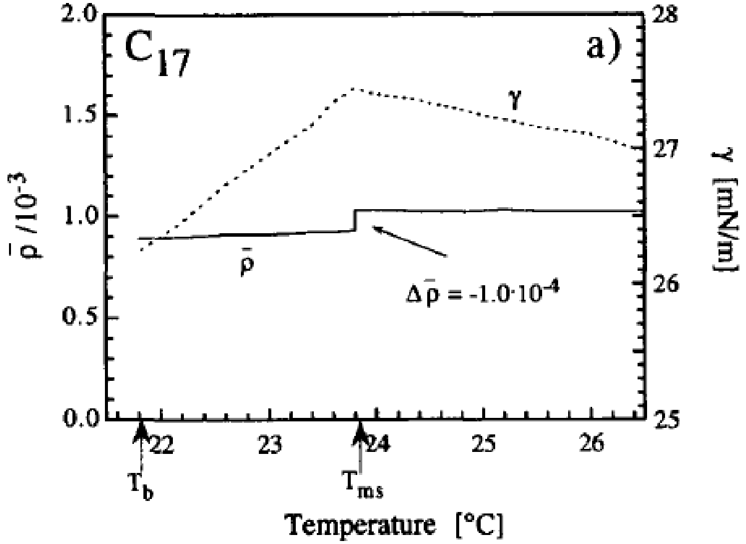
Approximating the integrals by the layer thickness d

$$\eta_{\mathrm{d}} = d[(\epsilon_z - \epsilon_1)(\epsilon_z - \epsilon_2)/\epsilon_z], \tag{3}$$

$$\eta_{\mathrm{a}} = d(\epsilon_x - \epsilon_z). \tag{4}$$

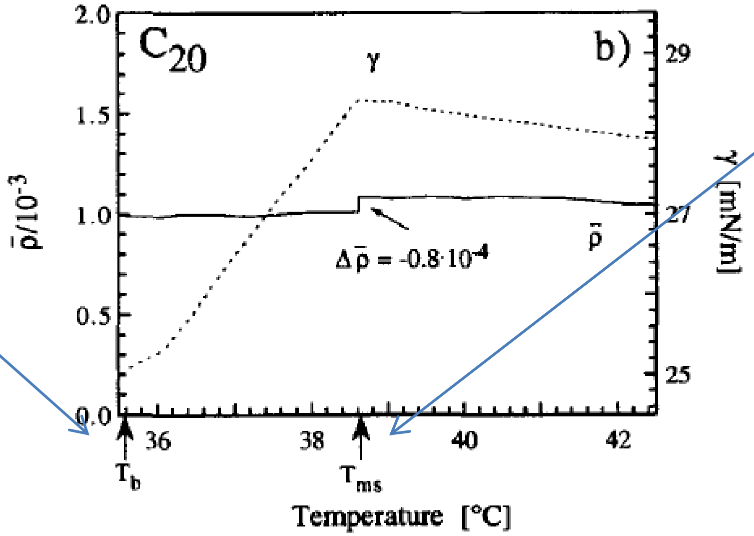
Result

Sample – Alkane ($C_n = CH_3(CH_2)_{n-2}CH_3$) ← n = 17, 20 and 36



Surface phase transition temp.

Above the bulk melting temp.



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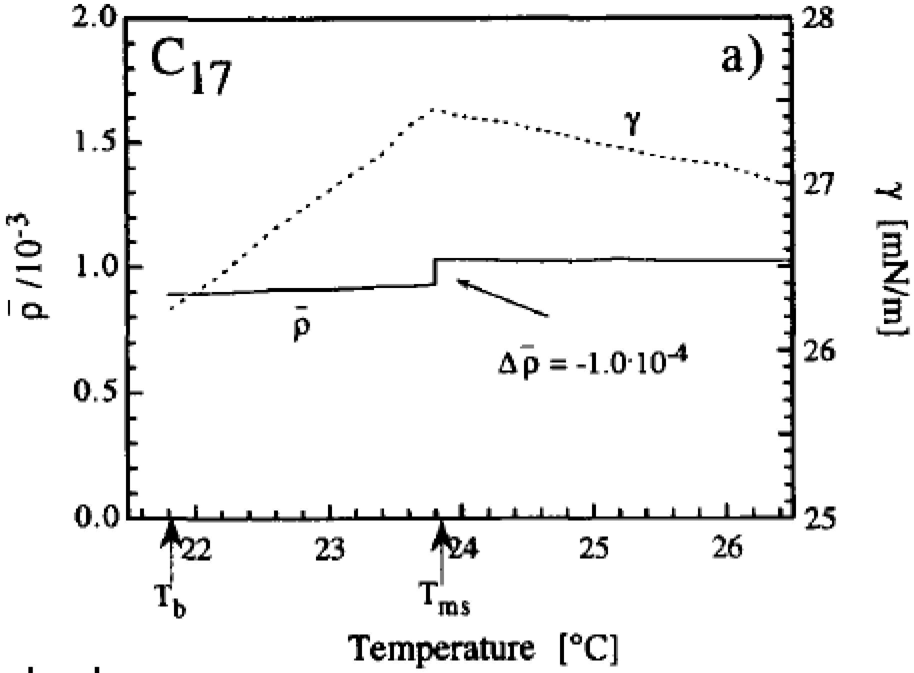
Interface profile proposed by X-ray study



Densely packed alkane monolayer

Unstructure!!

X-ray studies have proposed

Interface profile proposed by X-ray study

η is due to only to surface roughness. (above T_{ms})

ε_1 = 1.00 (air) and ε_2=2.05 (typical of an isotropic liquid alkane phase) and measured value $\rho = 1\times 10^{-3}$

We obtained with eq. (1) and (2) : $\eta_d = -0.12nm \quad t \approx 0.70nm$

$$\boxed{\eta = \frac{\lambda}{\pi}\frac{(\epsilon_1 - \epsilon_2)}{\sqrt{\epsilon_1 + \epsilon_2}}\bar{\rho}.} \qquad (1)$$

X-ray data is 0.43 nm

$$\begin{aligned}\eta &= \eta_r + \eta_d + \eta_a \\ &= \boxed{\frac{t}{4.394}(\epsilon_1 - \epsilon_2)\ln\left(\frac{\epsilon_2}{\epsilon_1}\right)} \\ &\quad + \int dz \frac{[\epsilon_z(z) - \epsilon_1][\epsilon_z(z) - \epsilon_2]}{\epsilon_z(z)} \\ &\quad + \int dz [\epsilon_x(z) - \epsilon_z(z)]. \qquad (2)\end{aligned}$$

Interface profile proposed by X-ray study

below T_{ms}

X-ray data is increased in the electron density in the surface layer of about 20%

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Using the Clausius-Mossotti relationship $\gamma_{mol} = \frac{3}{N}\left(\frac{\varepsilon/\varepsilon_0 - 1}{\varepsilon/\varepsilon_0 + 2}\right)$

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Density increase obtain $\varepsilon_z(T < T_{ms}) = 2.35$

η is due to only to density increase (below T_{ms}) and layer thickness 2.5 nm

Using eq.3 $\eta_d = 0.43nm$

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BUT

According to eq. (1) $\bar{\rho} = -6.4\times10^{-3}$ ➡ $\Delta\rho \approx 6.4\times10^{-3}$

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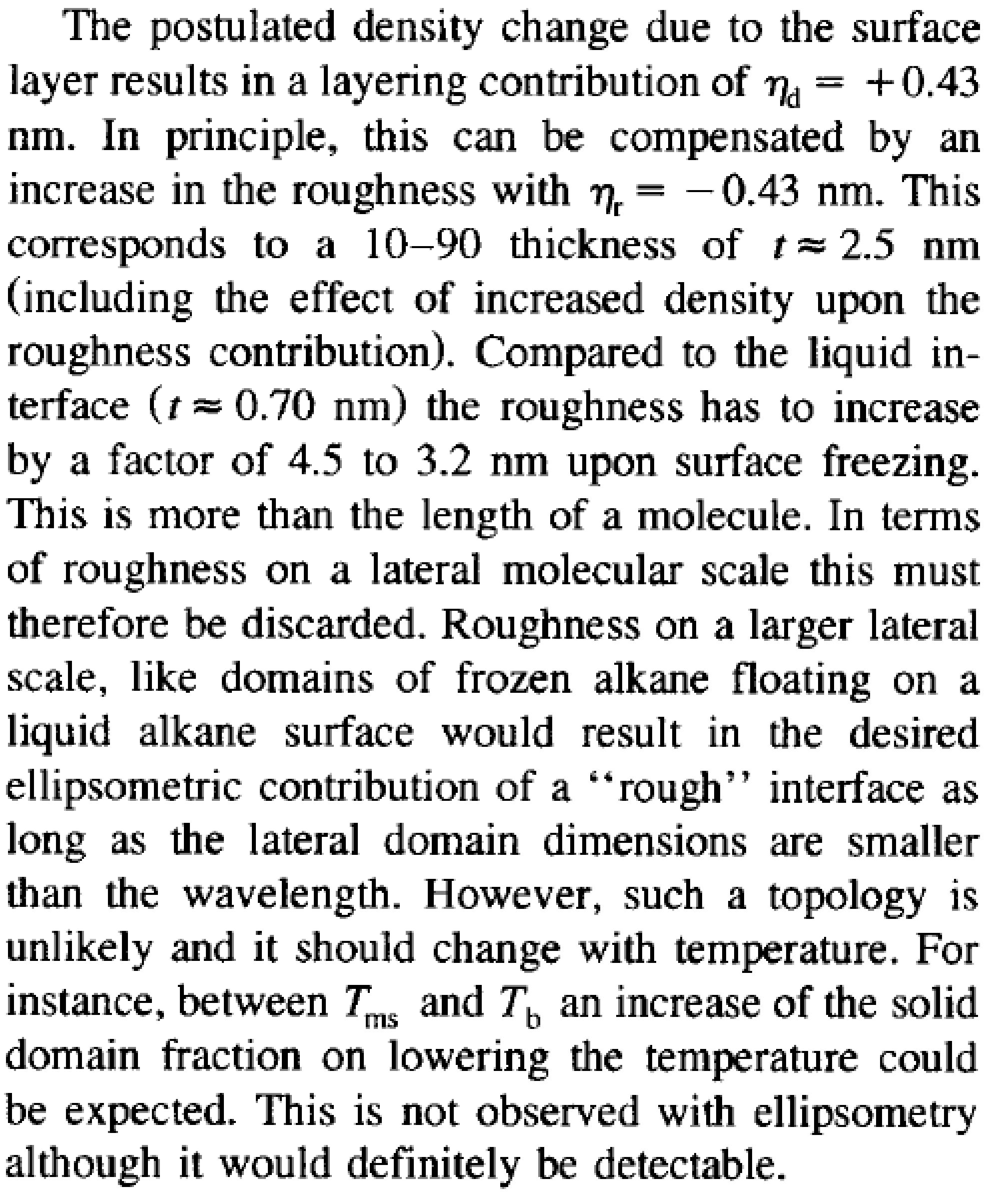
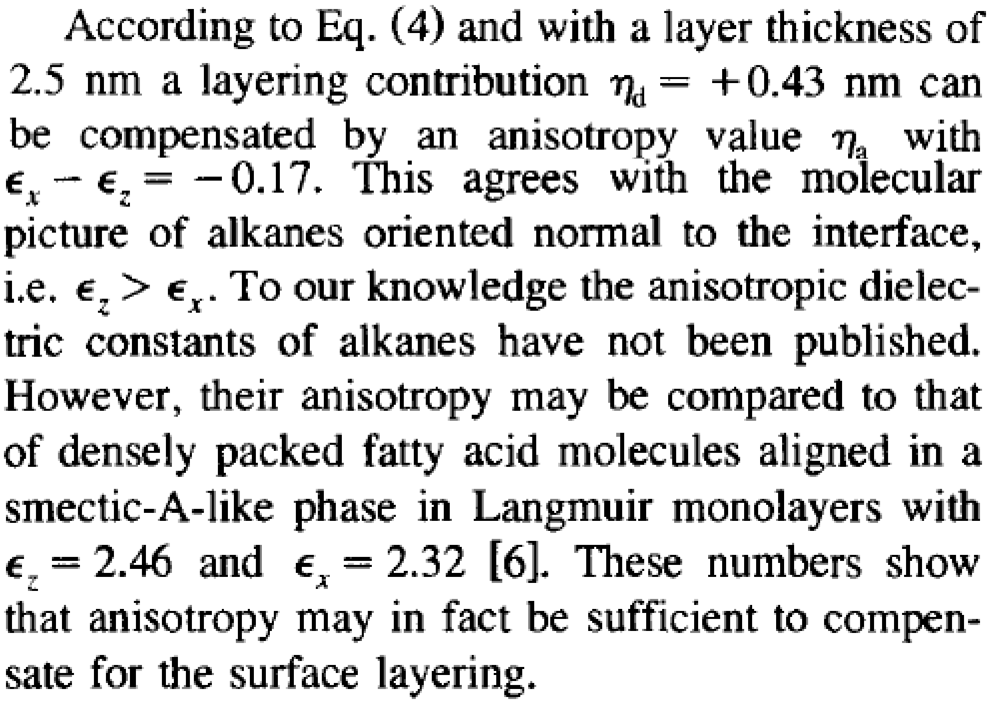
Compensation of layering by roughness



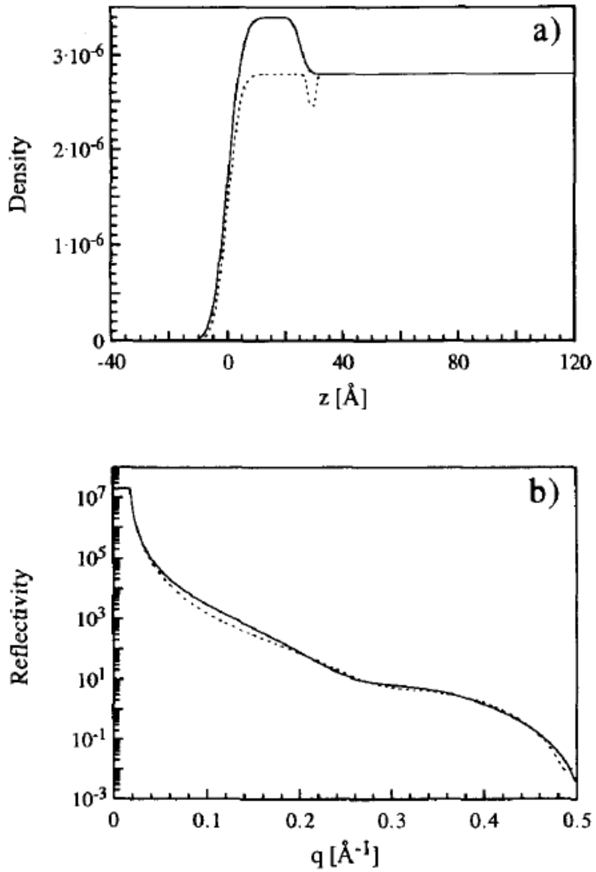
The postulated density change due to the surface layer results in a layering contribution of $\eta_d = +0.43$ nm. In principle, this can be compensated by an increase in the roughness with $\eta_r = -0.43$ nm. This corresponds to a 10–90 thickness of $t \approx 2.5$ nm (including the effect of increased density upon the roughness contribution). Compared to the liquid interface ($t \approx 0.70$ nm) the roughness has to increase by a factor of 4.5 to 3.2 nm upon surface freezing. This is more than the length of a molecule. In terms of roughness on a lateral molecular scale this must therefore be discarded. Roughness on a larger lateral scale, like domains of frozen alkane floating on a liquid alkane surface would result in the desired ellipsometric contribution of a ‘‘rough’’ interface as long as the lateral domain dimensions are smaller than the wavelength. However, such a topology is unlikely and it should change with temperature. For instance, between T_{ms} and T_b an increase of the solid domain fraction on lowering the temperature could be expected. This is not observed with ellipsometry although it would definitely be detectable.

Compensation of layering by anisotropy



According to Eq. (4) and with a layer thickness of 2.5 nm a layering contribution $\eta_{\mathrm{d}} = +0.43$ nm can be compensated by an anisotropy value η_{a} with $\epsilon_x - \epsilon_z = -0.17$. This agrees with the molecular picture of alkanes oriented normal to the interface, i.e. $\epsilon_z > \epsilon_x$. To our knowledge the anisotropic dielectric constants of alkanes have not been published. However, their anisotropy may be compared to that of densely packed fatty acid molecules aligned in a smectic-A-like phase in Langmuir monolayers with $\epsilon_z = 2.46$ and $\epsilon_x = 2.32$ [6]. These numbers show that anisotropy may in fact be sufficient to compensate for the surface layering.

Alternative interface structure model



g. 2. Two possible electron density profiles (a) and their corre- onding similar X-ray reflectivities (b) for surface frozen kane/air interfaces. The full lines exemplify the model of a ystalline surface monolayer with an increased electron density at e interface. The dotted lines represent the model of a smectic-like onolayer ordering with identical electron densities in the surface yer and in the bulk. In this case the X-ray interferences originate om a density gap between the monolayer and the bulk.

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