Thickness of Slag Bubble Films by Laser Absorption

S Sun, C Nexhip and S Jahanshahi

G K Williams Cooperative Research Centre

CSIRO Division of Minerals, Box 312, Clayton South, Vic. 3169, Australia

Slag foaming is a critical phenomenon in a range of smelting processes. Recently, attempts have been made in characterising the slag bubble films and in determining the mode and the rate of liquid draining. The laser absorption data were analysed in the present work to show the variation with time of the thickness of slag films of the CaO-SiO_2-Al_2O_3-Fe_2O_3-P_2O_5 melt. The oscillating intensity of the transmitted light was attributed to the Fabry-Perot type interference (transmission modulated by multiple reflection within the film) of the coherent laser light. Towards the end of draining, the film was most likely thinning down to approximately 0.02 μm (20 nm). The electrical double layer repulsion was discussed and the calculation showed that with film thickness down to 20 nm, this repulsive force may start to play some role in stabilising slag foams.

Slag foaming has direct operational impact in the BOF and the EAF steelmaking and in various bath smelting processes. It has naturally attracted wide and continual research interest. Despite the effort, some of the fundamental questions are still eluding definite answers. For instance, what is the typical bubble film thickness? How does liquid drain in the bubble films? The present authors have recently devised techniques for the study of liquid slag films spanning on a Pt wire frame withdrawn from a molten slag pool [1-2]. Laser interference and absorption techniques have been used to determine the thickness of slag films. The laser absorption data show an oscillating behaviour. These data have been analysed in the present work. The possible effect of double layer repulsion is also discussed.

Theory

When a beam of coherent light shines on the surface of a film, part of the light will reflect and part will be transmitted. Assuming the surface has a reflectivity of R and a transmission coefficient of t (= 1 – R), the reflected beam will have an intensity of $I_0 R$ and the transmitted $I_0 t$. When the transmitted light hits the back surface of the film, similar things will happen. The internally reflected beam from the back surface will be reflected again at the front surface to travel in the original direction, leading to secondary transmission, and so forth. Each round of double reflection will result in a phase lag of $(4\pi nL/l)$ and an attenuation of the intensity by a factor of e^{-2aL}, where l is the wavelength of the light, L is the thickness of the film, n is the refractive index and a the absorption coefficient of the film material.

Following similar procedures for deriving the Fabry-Perot interference formula [3], but including the attenuation factor, the following formula may be obtained for the light intensity transmitted through the film:

$$I_t = \frac{I_0 (1-R)\ e^{-aL}}{(1-R\ e^{-aL})^2 + 4R\ e^{-aL} \sin^2(2pnL/l)} \tag{1}$$

Equation (1) is a general formula for normal incidence of coherent light beam on a thin film. If there is no attenuation through the film, the equation reduces to the usual Airy's formula for multi-reflection interference [3], i.e.,

$$I_t = \frac{I_0}{1 + [\,4R/(1-R)^2\,]\sin^2(2pnL\,/\,l\,)} \qquad (2)$$

For incoherent light, there will be a random distribution of phase angle at any given point. Assuming this distribution is uniform, Equation (1) may be integrated over the phase angle to obtain the average intensity,

$$I_t = \frac{I_0\,(1-R)\;e^{-aL}}{1-R^2\;\;e^{-2aL}} \qquad (3)$$

This equation is identical to that given in Slag Atlas [4] for normal optical absorption. If the surface is highly transmissive therefore *R* approaches zero, then both Equations (1) and (3) will reduce to the common Lambert's law form:

$$I_t = I_0\,e^{\,-aL} \qquad (4)$$

As can be seen from Equation (1), the intensity of the transmitted light will decrease with increasing film thickness, but will be modulated by the second term in the denominator. The intensity will oscillate depending on whether the internally reflected beam is in phase or out of phase with the primary transmitting beam. It goes through cycles as the optical thickness (nL) of the film changes by half wavelengths ($nL = 0.5\;l$ leading to a lag in phase angle by $2\pi nL/l = \pi$).

Laser Absorption Analysis

The authors have recently developed new techniques for the study of slag film draining. This has been used to determine the rate of liquid draining in a molten slag film spanning a platinum wire frame drawn from a slag bath. Laser interferometry and absorption have also been used to estimate the film thickness [1-2]. A He-Ne laser source was used for the absorption studies and the wavelength of the laser was 633 nm.

In Figure 1, an example of the absorption curve is shown for a slag of 1.3% P_2O_5, 15% Al_2O_3, 9.6% Fe_2O_3 with CaO/SiO_2=0.6 (All percentage numbers for composition refer to mass% in this article). The experiment was carried out in air at 1573K. It is clearly seen that, as the film thins, the absorption oscillates before it finally settles between 0.001 – 0.002 (0.1 – 0.2 %). Repeated experiments gave results showing similar behaviour (Figure 2). The low absorption limit (before rupture) is between 0.001 and 0.005 (0.1 and 0.5 %), with an average of approximately 0.002 (0.2 %). The initial part (thick film limit) averages to about 0.015 (1.5%). During the 30 seconds of draining, the intensity of the transmitted beam oscillates for about 3 cycles. It was observed that towards the end, the film always turns black in each experiment.

These data have been analysed using the Lambert's law (Equation 4) [2]. With the value of a of 7.6 mm^{-1} (obtained for solidified slags of CaO/SiO_2=0.5 – 1.5 and 10% Fe_2O_3 [5]), the film thickness was calculated to be 0.2 to 3 μm in the flat central part of the film [2]. In particular, the thickness before rupture was given as 0.2 μm.

As shown in the previous section, the Lambert's law does not account for the reflection of the light at the front and the back surfaces. For thin films, this could be a major part of the loss in transmission. It is also difficult to explain the intensity oscillation using Lambert's law. Although it could be attributed to oscillations or fluctuations in film thickness, for the type of slags tested, there is no other evidence to support it. For instance, the interference pattern usually shifts uniformly, instead of moving back and forth as would be expected for thickness oscillation.

Since the light source is coherent, interference is expected, at least for thin films. A more appropriate account of the light intensity of the transmitted beam is Equation 1, in which the effect of the phase angle is incorporated.

The solid line in Figure 3 shows how the intensity of the transmitted beam varies with film thickness with a = 7.6 mm^{-1} and R = 0.005 (0.5%). The dot-dashed line illustrates the Lambert's law behaviour. It can be seen that Lambert's law represents only the upper envelope of the true transmission. The dashed line shows the incoherent limit (Equation 3). The coherence of a beam is expected to deteriorate with film thickness and with surface roughness. So for initial thick films, the transmission may approach the incoherence limit.

Figures 4 and 5 illustrate how the transmission versus thickness is influenced by a and by R. As is expected, a determines the rate of attenuation and R the magnitude of oscillation ($4R$ peak-to-peak) within the short thickness range.

The oscillation of the observed intensity of the transmitted beam could therefore be easily accounted for by the multi-reflection interference discussed here. What is not easily determined is whether the observed end point in the draining experiment is due to the primary peak, therefore L of 0.02 μm, or due to the secondary or tertiary peak, and L of 0.2 or 0.4 μm, respectively. However, the observation that, in the final stage of draining, the film always turns black may imply that the transmission peak before rupture is the primary one rather than the higher order ones. Therefore the film is most likely draining from 0.1 μm to 0.02 μm in the final stage.

A Discussion on Double Layer Repulsion

The repulsion between electrical double layers has been identified, among other things, as a factor controlling or at least contributing to slag foam stability [6]. For thin films of aqueous electrolyte solutions, there have been various investigations into the double layer repulsion [7a]. For molten slags, there has not been any detailed discussion on it. This may have partly been because of the lack of information about the actual thickness of slag foam films. An attempt is made here to estimate this force in a typical slag system.

For two flat double layers, Verwey and Overbeek [7b] have made a thorough analysis of the interactions and have established the procedures for the calculation of the force or the interaction energy for overlapping double layers.

Assume the surface potential of the double layer is Y_0, and the potential at the mid-point within the film is Y_m. For small Y_m, i.e., $(z\ e\ Y_m / \varepsilon_r\ \varepsilon_0\ k\ T) << 1$, the repulsion pressure may be approximated by

$$p_{dl} = (e_r\ e_0\ k^2/2)\ Y_m^2 \qquad (5)$$

As would be expected, Y_m depends strongly on the thickness of the film, D,

$$Y_m = (8\ k\ T / z\ e)\ Z\ \exp(-kD/2) \qquad (6)$$

and

$$Z = \tanh(z e \Psi_0 / 4kT) \qquad (7)$$

For the calculation of p_{dl} using Equation 5, information of the relative dielectric constant, ε_r, the potential Ψ_m, and the Debye length, κ^{-1}, is required. The Debye length is defined as

$$L_D = \kappa^{-1} = (\varepsilon_r \varepsilon_0 kT / \Sigma n_i (z_i e)^2)^{1/2} \qquad (8)$$

For a 1 M 1:1 aqueous electrolyte solution, L_D is about 0.3 nm. Depending on the type of the solution and the concentration of the electrolyte, L_D may vary from less than 1 nm to about 100 nm for colloid systems [7a].

Calculations for molten slags are very difficult for a lack of relevant data. An attempt will be made here to estimate the magnitude of the interactions. The dielectric constant for slags is not known. For a variety of oxides [8], ε_r varies between 5 and 10 and for rutile (TiO_2) it is 86. For borosilicate glasses [8], ε_r is approximately 5. For the slag investigated, a value of ε_r of 10 is assumed. One school of thought regards a molten slag as predominantly ionic. In that case L_D would be less than 0.1 nm and the meaning of screening becomes irrelevant. This may mean that the theory is not valid for the molten slag, or the slag is not fully ionised in the sense of its ionic strength. At 1600K, assuming 0.1% of the oxide is ionised (into doubly charged cations and anions), the Debye length L_D is estimated to be 0.6 nm. If the ionisation ratio is 0.1 ppm, then L_D will be approximately 50 nm.

Following Verwey and Overbeek's procedure [7b], p_{dl} was calculated for L_D of 0.5, 1 and 2 nm as shown in Figure 6. The surface potential Ψ_0 was taken as 0.275 V. Sun and Belton's study on the effect of surfactant on gas-slag reaction kinetics suggests that the surface potential of liquid iron oxide could change by 0.12 V with small addition of P_2O_5 [9]. A surface potential of the order of 0.275 V does not appear unreasonable. However, it may be noted that the pressure p_{dl} is not very sensitive to the value of the surface potential except when the film is very thin and the double layer overlapping is substantial. As shown in Figure 6, the repulsion pressure between the two surfaces increases as the thickness D decreases. Also plotted in this figure is the equivalent pressure due to the Plateau border suction, $p = 2\sigma / r$, calculated by assuming the surface tension σ to be 0.5 N/m and the radius of curvature r to be 1 mm. The Plateau border suction is equivalent to a pressure of about 1000 Pa. Similar plots are given for Y_0 of 0.55 V in Figure 7. The general feature remains the same. The pressure for a given double layer separation may be two times higher than with Y_0 = 0.275 V. In both cases, the repulsive force is very sensitive to the film thickness or the double layer separation. As seen from Figures 6 and 7, by halving the thickness, the force increases by over 4 orders of magnitude.

As suggested previously, the Plateau border suction could be the dominant driving force for slag film thinning [1,2]. The plot in Figure 6 shows that if the film thins down to 3 – 10 nm, the double layer repulsion could be strong enough to balance the driving force for thinning. For the slags studied in this work, the film thickness gets down to about 20 nm. This is probably into the regime where the double layer repulsion starts to play a role in stabilising slag foams.

Conclusion

The oscillating intensity of the transmitted laser beam through thin films of the slag of 1.3% P_2O_5, 15% Al_2O_3, 9.6% Fe_2O_3 with CaO/SiO_2=0.6 at 1573K could be accounted for by the interference of the coherent beam through multiple internal reflection within the slag film. The absolute thickness of the film was not unequivocally determined, but was most likely thinning from 100 nm (0.1 μm) down to 20 nm (0.02 μm) in the final stage of draining before film rupture.

The repulsive force between the two double layers of a thin film of slags has been estimated. For slags with a Debye length (characteristic distance for ionic screening) of 0.5 – 2 nm, this force is negligible compared to the Plateau border suction for most part of the life of the thinning film. Towards the end of draining, with the film thickness approaching 20 nm, the electrical double layer repulsion may start to play a role in stabilising slag foams.

List of Symbols

D	Film thickness; double layer separation
I_0	Intensity of the incident beam

I_t Intensity of the transmitted beam

k Boltzmann constant

L Film thickness

L_D Debye length

n Refractive index

n_i Number density of ionic species in a solution

p_{dl} Repulsion force per unit area between double layers

r Principal radius of curvature

R Reflectivity of a surface

t Transmissivity of a surface $t = 1 - R$

T Temperature

z Number of charges on a cation or anion

z_i Number of charges on the ith cation or anion

a Absorption coefficient

e_0 Permeability of vacuum

e_r Dielectric constant

k Reciprocal of Debye length $L_D = 1/k$

l Wavelength of the laser beam

Y_0 Surface potential

Y_m Potential midway in a thin film

s Surface tension

Acknowledgment

The work is supported by the Australian Government Cooperative Research Centre Program through the G K Williams Cooperative Research Centre for Extractive Metallurgy, a joint venture between the CSIRO Division of Minerals and the Department of Chemical Engineering, the University of Melbourne.

Reference

1. C Nexhip, S Sun and S Jahanshahi, Proc. 5th Int. Conf. Molten Slags, Fluxes and Salts, Sydney, ISS, Warrendale, 1997, pp.297-306.
2. C Nexhip, S Sun and S Jahanshahi, Phil. Trans. R. Soc. Lond. A, 1998, Vol.356, pp.1003-12.
3. See for example: E Hecht, Optics, 2nd ed., Addison-Wesley, Reading, Massachusetts, 1987.
4. Slag Atlas, 2nd ed., Ed. By VDEh, Verlag Stahleisen GmbH, 1995.
5. M Susa, L Futao, and K Nagata, Proc 4th Intern Conf. On Molten Slags and Fluxes, ISIJ, Tokyo, 1992, pp.22-27.
6. D R Gaskell, Steel Research, 1989, Vol.60, pp.182-84.

7a. D J Shaw, Introduction to colloid and surface chemistry, 4th ed., Butterworths, Oxford, 1992.

7b. E J W Verwey and J Th G Overbeek, Theory of stability of lyophobic colloids, Elsevier, Amsterdam, 1948, cited in [7a].

8. Tables of Physical and Chemical Constants, Longmans, London, 13th ed, 1966.
9. S Sun and G R Belton, Met. Mat. Trans. B, 1998, Vol.29B, pp.137-45.

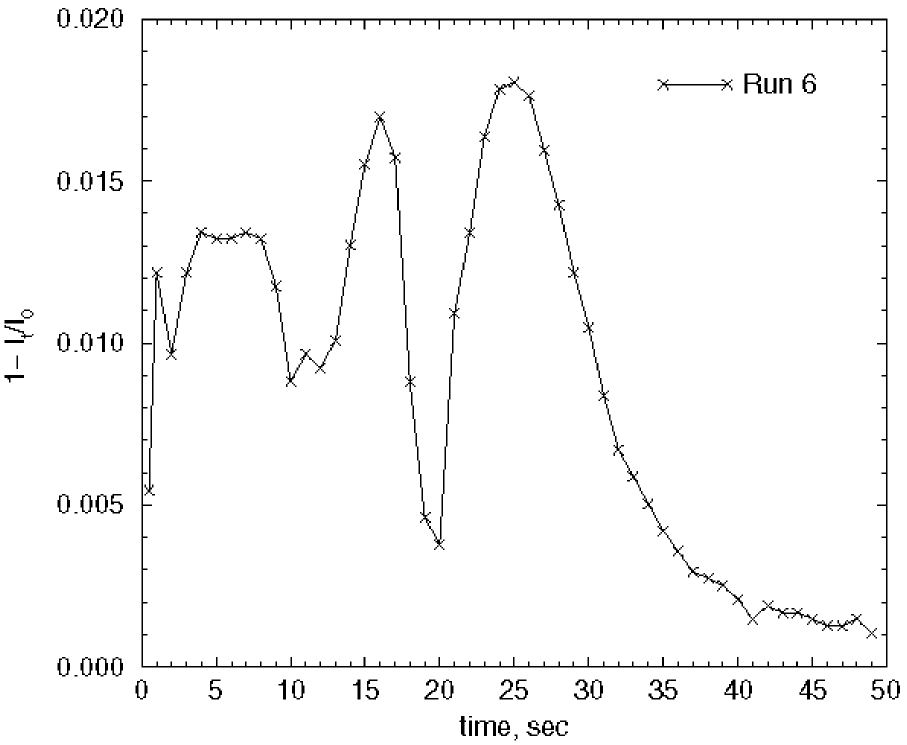

Figure 1 A typical relative intensity curve of the absorption of a laser beam through a liquid film of slag of 1.3% P_2O_5, 15% Al_2O_3, 9.6% Fe_2O_3 with CaO/SiO_2=0.6 at 1573K.

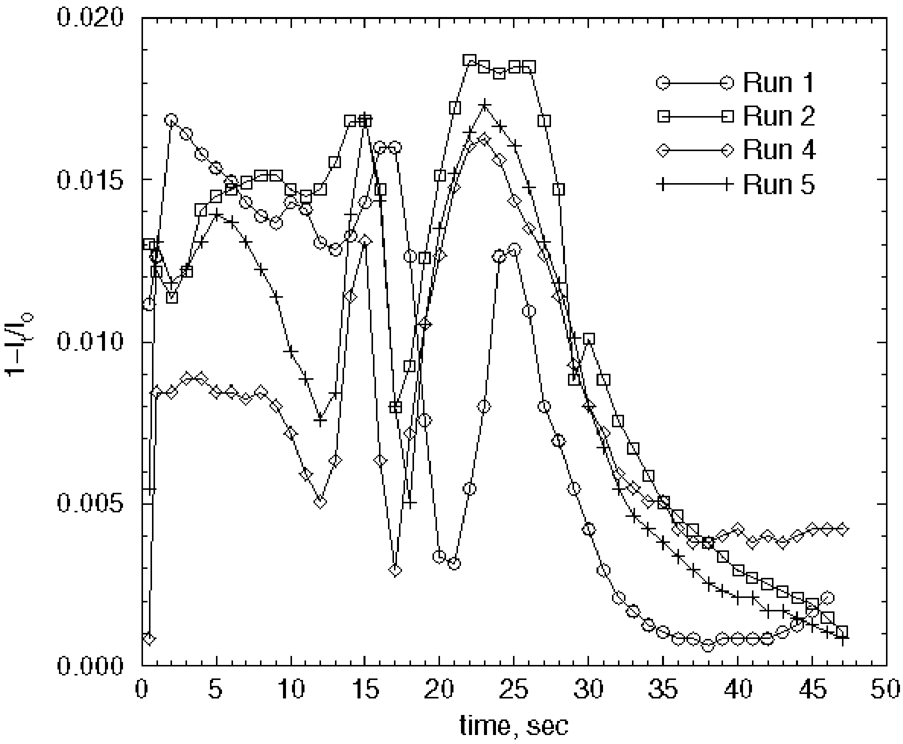

Figure 2 Results of the repeated measurements of the relative intensity curve of the absorption of a laser beam through a liquid film of slag of 1.3% P_2O_5, 15% Al_2O_3, 9.6% Fe_2O_3 with CaO/SiO_2=0.6 at 1573K.

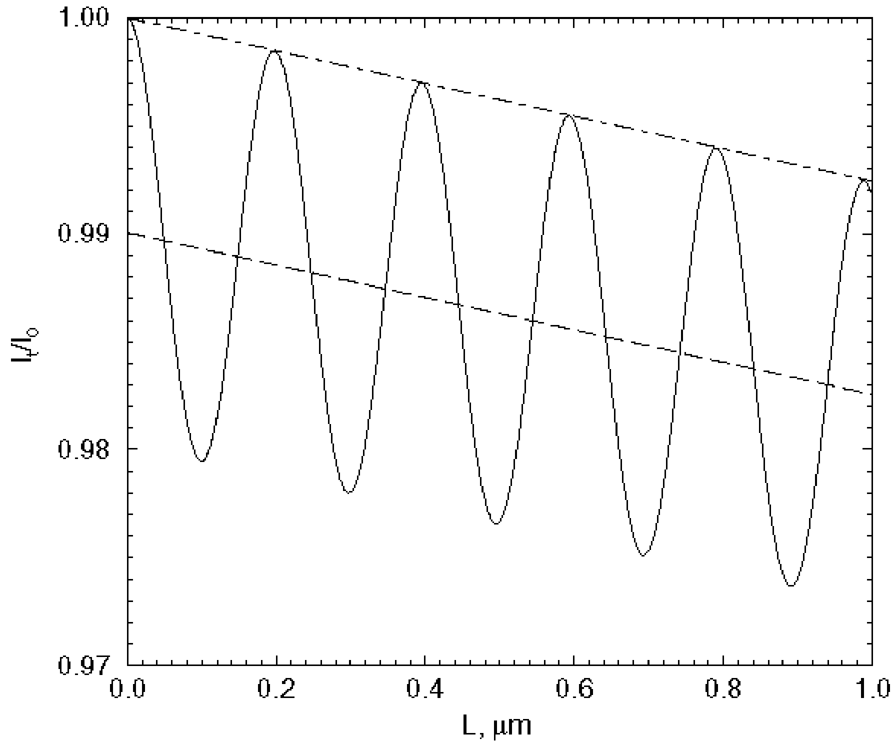

Figure 3 Plots illustrating the relative intensity of the transmitted laser beam through thin films (a = 7.6 mm^{-1}). Solid curve: coherent beam transmission; dashed line: incoherent beam transmission; dot-dashed line: Lambert's law limit (incoherent beam and no reflection).

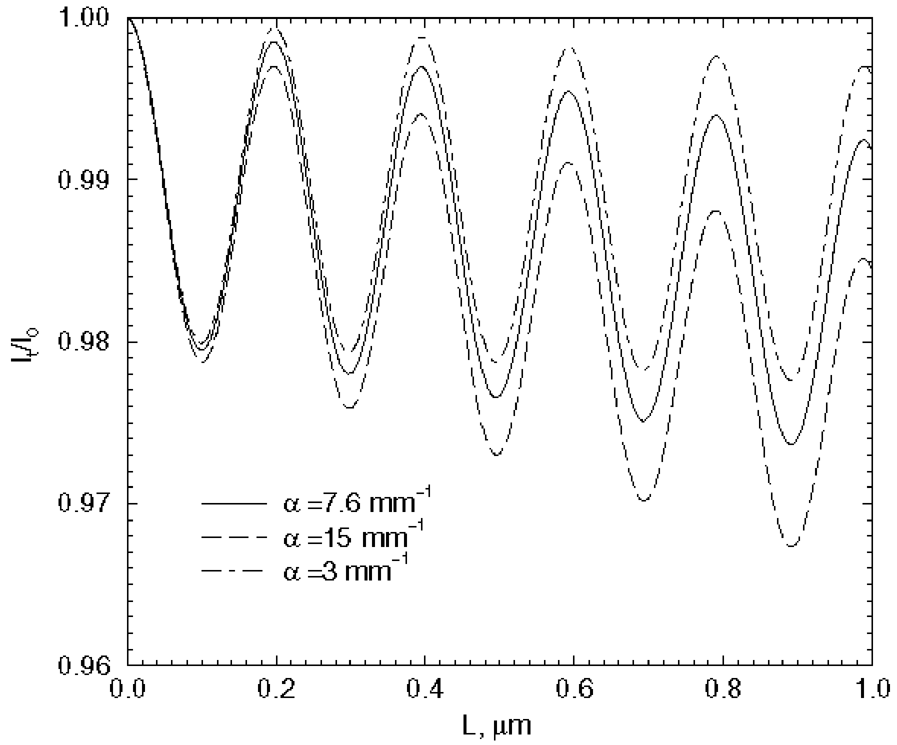

Figure 4 Plots of relative intensity versus thickness showing the effect of a.

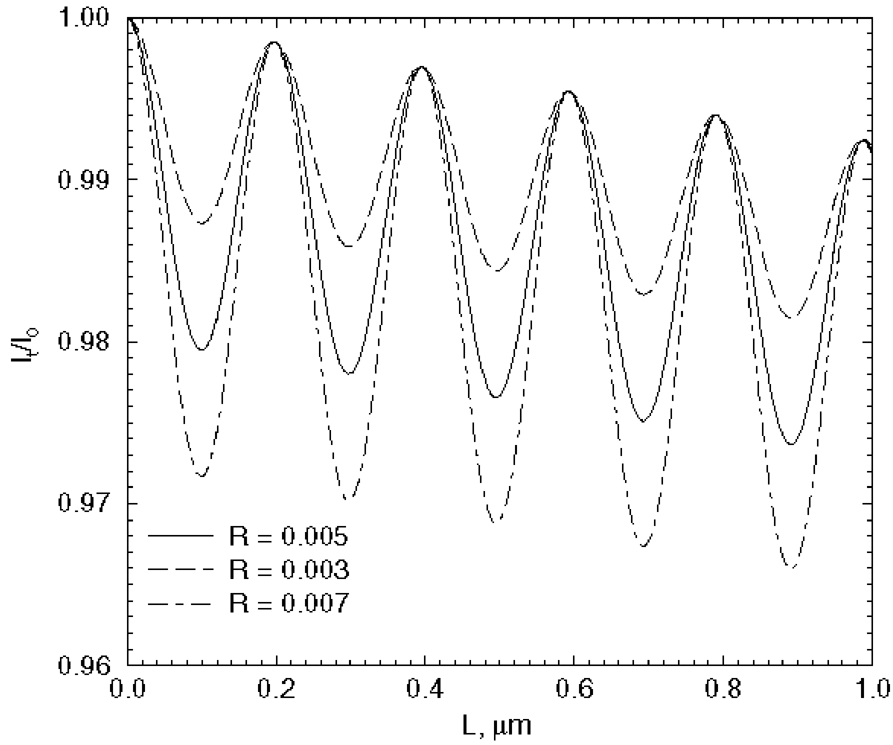

Figure 5 Plots of relative intensity versus thickness showing the effect of *R*.

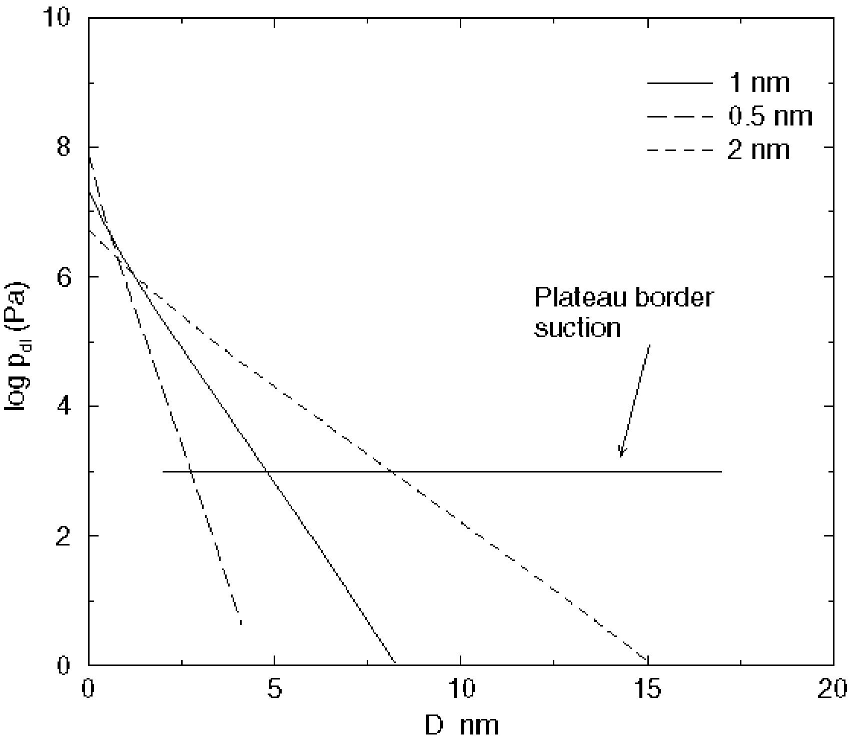

Figure 6 Calculated force of repulsion between two double layers of a thin film of thickness *D*. (Y_0 = 0.275 V)

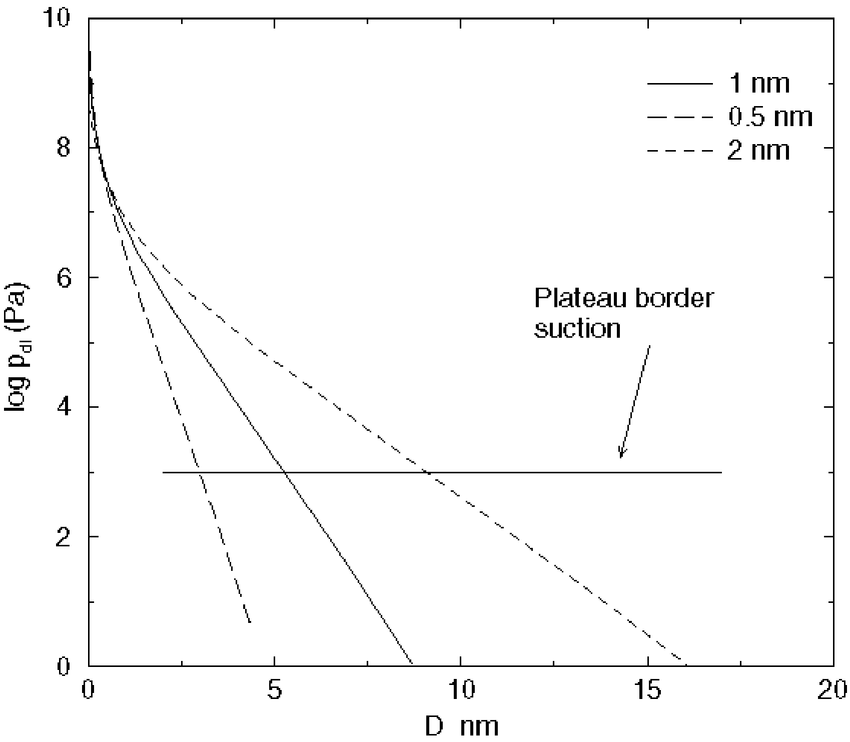

Figure 7 Calculated force of repulsion between two double layers of a thin film of thickness *D*. (Y_0 = 0.55 V)