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Measurement of the bending elastic modulus of a flat monolayer at a liquid interface

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Abstract. The bending elastic modulus of monolayers is deduced from the study of their thermal fluctuations on a low scale (about 100 Å) by optical techniques: x-ray reflectivity measurements and ellipsometry. We explain why ellipsometry is more sensitive than reflectivity at small scales.

1. Introduction

A monolayer at a flat liquid interface is constantly distorted by thermal fluctuations. There are three restoring forces: gravity, surface tension and bending elasticity. The energy required to overcome these forces is the sum of three terms:

$$E(q) = (S/2)(\Delta\rho\, g + \gamma q^2 + Kq^4)\zeta_q^2 \qquad (1)$$

where $\Delta\rho$ is the density difference between the two bulk phases, g is the acceleration due to gravity, γ is the interfacial tension, K is the bending elastic modulus of the monolayer and ζ_q^2 is the amplitude of a sinusoidal deformation of the wavevector $\boldsymbol{q}$ at the interface of area S. The measurement of the mean square amplitude $\overline{\zeta_q^2}$ of the thermal fluctuations provides information on the restoring forces on various scales.

(i) On a macroscopic scale (greater than 1 mm), i.e. at small q, the gravitational energy dominates.
(ii) On a microscopic scale (10–100 μm), i.e. at larger q, the capillary energy dominates.
(iii) On an ultra-microscopic scale (100 Å), i.e. at very large q, the curvature energy dominates.
(iv) On a molecular scale ($q > q_{\mathrm{mol}}$), the continuum model fails.

The intermediate (or microscopic) scale can be studied by surface light scattering [1] because this scale is close to but larger than the light wavelength λ ($q\lambda < 1$). On the ultra-microscopic scale ($q\lambda > 1$ for light), the scattered waves are evanescent and cannot be observed. This is typically the scale which could be explored by x-ray or neutron scattering, but in practice the refractive indices for these two types of radiation are close to unity and the scattered intensity is too low to be observed. A double-scattering experiment can fulfil the equation $q\lambda < 1$ with thermal modes of wavelength smaller than the wavelength of the light. In this case, $\boldsymbol{q} = \boldsymbol{q}_1 + \boldsymbol{q}_2$; the light is scattered first by a

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thermal mode of wavevector $\boldsymbol{q}_1$ and then by a thermal mode of wavevector $\boldsymbol{q}_2$. The simplest case is obtained by reflectivity measurements for which $\boldsymbol{q}_1 + \boldsymbol{q}_2 = \boldsymbol{0}$. In this case, the scattering vector $\boldsymbol{Q}_1$ is normal to the interface.

A simple model for monolayers at liquid interfaces makes a clear distinction between the roughness, i.e. the vertical position ζ of the interface above the point (x, y) of the horizontal plane, and the structure or thickness of the interfaces, i.e. the variation in the refractive index along the vertical axis $n(z - \zeta)$. The function n is assumed to be a characteristic of the monolayer, independent of the roughness ζ. With this model, the origin of the roughness of a monolayer at a liquid interface on a scale larger than the molecular scale is thermal fluctuations.

2. Reflectivity measurements

The reflected field $\boldsymbol{E}^{\mathrm{r}}_{mn}$ of polarization m, is related to the incident field $\boldsymbol{E}^{\mathrm{i}}_{n}$ of polarization n through the matrix elements $r_{mn}(\theta)$ for the reflection:

$$E^{\mathrm{r}}_{mn} = r_{mn}(\theta) E^{\mathrm{i}}_{n} \tag{2}$$

where θ is the incident angle and m, n are equal to s or p according to whether the polarization is perpendicular to or in the plane of incidence. For Fresnel interfaces, i.e. interfaces without thickness and without roughness (the refractive index is n_1 for $z > 0$ and n_2 for $z < n$; $\zeta = 0$), $r_{\mathrm{ps}} = r_{\mathrm{sp}} = 0$ and the diagonal terms are denoted r^{F}_{nn}.

Two different reflectivity techniques are used: reflected-intensity measurements and ellipsometry. The first technique measures only the light intensities, i.e. $|r_{nn}(\theta)|^2$, and loses the phase retardation at reflection. An interesting quantity is the ratio $R = |r_{nn}(\theta)|^2 / |r^{\mathrm{F}}_{nn}(\theta)|^2$, because it is equal to unity for a Fresnel interface and its deviation from unity gives information on the thickness and roughness of the studied interface. Ellipsometry gives information on the phase retardation at the reflection through the ratio

$$\rho_{\mathrm{e}} = (r_{\mathrm{pp}} + r_{\mathrm{ps}})/(r_{\mathrm{ss}} + r_{\mathrm{sp}}). \tag{3}$$

Monolayers at liquid interfaces are much thinner than the wavelength of the light; the denominator of equation (3) is equal to $r^{\mathrm{F}}_{\mathrm{ss}}$ to a good approximation. For a Fresnel interface, $\rho_{\mathrm{e}} = 1$ if $\theta = 0$, $\rho_{\mathrm{e}} = -1$ if $\theta = \pi/2$; there is an angle called the Brewster angle θ_{B} at which $\rho_{\mathrm{e}} = 0$. For real interfaces, ρ_{e} is a complex number. At the Brewster angle $\mathrm{Re}(\rho_{\mathrm{e}}) = 0$ and $\mathrm{Im}(\rho_{\mathrm{e}}) = \bar{\rho}$ is the ellipticity of the reflected light. $\bar{\rho}$ yields information on the roughness and the thickness of the interface. It is a very sensitive technique because it measures the deviation from zero: for a Fresnel interface, $\bar{\rho} = 0$ and, for a rough and thick interface, $\bar{\rho} \neq 0$.

In order to simplify this paper, we consider only the case of interfaces without thickness. It is not difficult to take into account the thickness of real interfaces.

In the case of large-scale roughness ($q\lambda \ll 1$), with a small slope ($q\zeta_q \ll 1$), each element dS of the interface reflects the light with a phase factor $\exp(\mathrm{i}Q_1\zeta)$:

$$r_{nn}(\theta) = r^{\mathrm{F}}_{nn}(\theta) \frac{1}{A} \int_A \exp(\mathrm{i}Q_1\zeta)\, \mathrm{d}A. \tag{4}$$

A is the area of the projection of the interface on the horizontal plane. If ζ is a Gaussian function [2]:

$$|r_{nn}(\theta)|^2 = |r^{\mathrm{F}}_{nn}(\theta)|^2 \exp(-Q_1^2\overline{\zeta^2}). \tag{5}$$

In the case of roughness on a small scale ($q\lambda \gg 1$), the electromagnetic wave propagates in a medium with a refractive index changing on a scale smaller than the wavelength λ and sees as a first approximation an average index [3, 4]

$$n(z) = \langle n_1[1 - Y(z - \zeta)] + n_2 Y(z - \zeta)\rangle_{x,y} \tag{6}$$

where $Y(z) = 1$ if $\zeta > z$ and $Y(z) = 0$ if $\zeta < z$. The reflectivity of the interface can be calculated as the reflectivity of a thick interface with a refractive index $n(z)$. The reflected wave is the sum of plane waves reflected at different levels inside the interface. If ζ is a Gaussian function, the reflectivity is given by equation (5) in which Q_1Q_2 take the place of Q_1^2 because in this model the incident and reflected waves propagate into the interface with an average index n_1n_2.

The demonstration of equation (5) neglects some effects limiting its validity. First, the local variation in the incidence angle due to the slope of the roughness is not taken into account in the calculation of the interfacial reflectivity. This assumes that the variation in the Fresnel reflectivity $r^{\mathrm{F}}_{nn}(\theta)$ with θ is small. This approximation is rough in the vicinity of the critical total refraction angle where the Fresnel reflectivity varies greatly for a small variation in the incidence angle. Secondly, the calculation supposes that the electromagnetic waves propagate as plane waves, without deformation, in the vicinity of the rough interface. This is valid in the case where the deformation introduced by the rough interface can be neglected ($|n_1 - n_2| \ll n_1$). This is the case for interfaces in the vicinity of a critical point [3, 4] or for interfaces studied with x-rays [5].

Equation (4) or (5) fails for p polarization in the vicinity of Brewster's angle. In this case, the incident plane wave induces dipolar moments in the medium, which point in the direction of the specular reflection. (At the Brewster angle, the direction of the transmitted light and the direction of the specular reflection are perpendicular.) The Fresnel reflectivity vanishes: $r^{\mathrm{F}}_{\mathrm{pp}}(\theta_{\mathrm{B}}) = 0$. The origin of the small reflectivity of a rough interface at Brewster's angle for the p polarization is the deformation of the electromagnetic field in the vicinity of the interface which induces dipolar moments, with the direction of each moment scattered around the direction of reflection. For a roughness of single mode ζ_q with a weak slope and very high wavevector q ($q\lambda \gg 1$), the phase retardation due to the roughness can be neglected; the solution for the deformation of the electromagnetic field is electrostatic with only one characteristic length—that introduced by the mode q [8]. The greater the index difference $n_1 - n_2$ and the interfacial slope $q\zeta_q$, the larger is the field deformation. An electrostatic solution for a mode q/m, $m\zeta_q$ can be deduced from an electrostatic solution for a mode q, ζ_q, through a similarity transformation of ratio m. In the two cases, the deformations of the electric field are the same, but the volumes of the spaces occupied by the deformed field are in the ratio m; consequently, the reflected field is proportional to ζ_q. At second and lowest order in ζ_q, one obtains

$$\bar{\rho} \sim [(n_1 - n_2)/\lambda] q\zeta_q^2. \tag{7}$$

A summation of (7) over q gives the ellipticity for an isotropic rough interface with roughness on a small scale (electrostatic approximation $q\lambda \gg 1$) [6, 7].

In conclusion, a reflected-intensity measurement is sensitive to phase retardation, which depends only upon the depth of the interfacial roughness: $\zeta^2 = \Sigma_q\, \zeta_q^2$. Ellipsometry is sensitive to the field deformation in the vicinity of the interface, a function of the slope of the interfacial roughness. The signal is proportional $\Sigma_q\, q\zeta_q^2$. Consequently,

ellipsometry is more sensitive to small-scale roughness than reflected-intensity measurements are and is more convenient for bending elasticity measurements.

3. A monolayer at a liquid interface

In the case of a monolayer at a liquid interface, the origin of the roughness for $q < q_{mol}$ is thermal fluctuations. For small fluctuations, the modes ζ_q are independent and the average energy of each mode is $k_B T/2$:

$$\overline{\zeta_q^2} = k_B T/(\Delta\rho\, g + \gamma q^2 + K q^4). \tag{8}$$

The interfacial roughness measured in a reflected-intensity measurement is obtained by the summation of equation (8) over all the thermal modes:

$$\overline{\zeta^2} \sim (1/\gamma)\ln(q_{max}/q_{min}) \tag{9}$$

where q_{min} is the cut-off at large scale introduced by the aperture of the instrument or by gravity. q_{max} is an upper cut-off which depends upon the values of the surface tension and the bending elasticity [9, 10]:

$$q_{max} = q_{mol} \quad \text{if} \quad q_{mol} \ll \sqrt{\gamma/K} \qquad q_{max} = \sqrt{\gamma/K} \quad \text{if} \quad q_{mol} \gg \sqrt{\gamma/K} \tag{10}$$

In the second case, the reflected intensity has a logarithmic dependence on K.

In ellipsometry and as a first approximation, the ellipticity is

$$\sum_q q\overline{\zeta_q^2} \sim \frac{1}{\gamma} q_{max}^e \tag{11}$$

with [9, 10]

$$q_{max}^e = q_{mol} \quad \text{if} \quad q_{mol} \ll (\pi/2)\sqrt{\gamma/K} \qquad q_{max}^e = (\pi/2)\sqrt{\gamma/K} \quad \text{if} \quad q_{mol} \gg (\pi/2)\sqrt{\gamma/K}. \tag{12}$$

In the second case, the ellipticity is inversely proportional to the square root of the bending elasticity and the greater part of the summation $\Sigma_q\, q\overline{\zeta_q^2}$ is obtained for q wavevectors close to q_{max}^e, where the capillary energy is equal to the curvature energy. q_{max} is the scale of measurement in ellipsometry. The two techniques are sensitive to the bending elasticity (but the signals are proportional to the logarithm of K and to the square root of K respectively) with the condition $q_{mol} \gg \sqrt{\gamma/K}$.

In the case of low interfacial tension and low bending elasticity as for some monolayers of soluble surfactant at the oil–water interface studied by ellipsometry, the thermal fluctuations are large and the approximation of independent modes (equation (8)) is not valid. If the coupling between modes is not too large, it can be taken into account through a renormalization of the parameters of equation (8).

(i) $\gamma \ll Kq^2$; the capillary energy can be neglected, and the bending elastic modulus K decreases with the scale q, following a universal function for $K > k_B T$ [11, 12]; it is a logarithmic decrease. For $K \leqslant k_B T$, it is more complicated because $K(q)$ is not a universal function; it must depend upon details of the system studied. In this case we use a simple model where K reaches a minimum positive value [9].

(ii) $\gamma \gg Kq^2$; the capillary energy dominates and the thermal modes are independent; the bending elastic modulus K is a constant K_∞ [9].

The deviation of the ellipticity from the values given by equations (11) and (12) and introduced by the scale dependence of K is too small to be observed experimentally.

4. Experimental procedure

In a reflectivity measurement on a real interface, the signal contains information about the roughness (the thermal fluctuations for a monolayer at a liquid interface) and about the structure of the interface; these two types of information are mixed. The reflectivity of a real interface is given by equation (5) in which the reflectivity of this real interface, in the absence of thermal fluctuations, takes the place of the Fresnel reflectivity $|r^{\mathrm{F}}_{nn}(\theta)|^2$. The reflectivity is the product of a roughness term and a structure term or form factor. The ellipticity measured in ellipsometry is the sum of two terms: a roughness term $\bar{\rho}^{\mathrm{R}}$ given by equation (11) or (12) and a structure term $\bar{\rho}^{\mathrm{L}}$ which includes the thickness [13] of the interface and its optical anisotropy [14]:

$$\bar{\rho} = \bar{\rho}^{\mathrm{R}} + \bar{\rho}^{\mathrm{L}}. \tag{13}$$

The experiment has to distinguish between the two contributions in a global measurement. The thermal fluctuations of a monolayer at a free surface of a liquid are too small to be observable with visible light. The technique which can be used is the reflected-intensity measurement of x-rays [5]. In this case, the form factor is an oscillating function of the angle of incidence, damped by the roughness term. The origin of the oscillations is the interference between the beams reflected at different levels in the monolayer. These oscillations give information on the structure of the interface, and the roughness $\overline{\zeta^2}$ is deduced from the damping and allows the bending elastic modulus to be calculated from equations (9) and (10) if $K > 100k_{\mathrm{B}}T$. The interesting experimental quantity is the product of the roughness and the surface tension: $\gamma\overline{\zeta^2} \sim \ln(\gamma/K)$. K is only obtained with a low accuracy because it appears in a logarithm.

The thermal fluctuations of a monolayer of small interfacial tension are large enough to be observed by ellipsometry. It is possible to distinguish between the roughness term $\bar{\rho}^{\mathrm{R}}$ and the structure term $\bar{\rho}^{\mathrm{L}}$ by varying one parameter which affects only one of the two terms. Some soluble surfactants give microemulsions when they are mixed with oil and water. The interfacial tension of a saturated monolayer of these surfactants at the oil–water interface is very low and a large variation in the interfacial tension occurs with a small variation in the ionic force of the water [15] (ionic surfactants) or the temperature [16] (non-ionic surfactants). The measured ellipticity for these monolayers has a pronounced peak at the same salinity or temperature as the minimum interfacial tension, indicating an increase in the thermal fluctuations for low γ. The ellipticity versus $1/\sqrt{\gamma}$ is a straight line as indicated by equations (11) and (12) (figure 1). The bending elastic modulus is deduced from the slope of this straight line. It must be remarked that the same surface tensions are obtained for two different salinities or temperatures. The ellipticities for these two different salinities or temperatures are the same, indicating that only the interfacial tension is modified by the small variation in the parameter (ionic force or temperature). The measured values of the bending elastic modulus for these monolayers are very low $K \sim k_{\mathrm{B}}T$ [10, 17, 18]; the coupling between modes has to be taken into account.

5. Conclusion

The study of thermal fluctuations on an ultra-microscopic scale (about 100 Å) by optical techniques is a method for measuring the mean bending elastic modulus of monolayers.

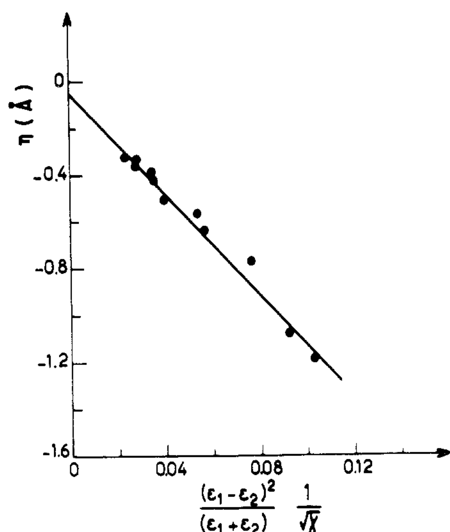

Figure 1. $\eta = (\pi/\lambda)[\sqrt{\varepsilon_1 + \varepsilon_2}/(\varepsilon_1 - \varepsilon_2)]\bar{\rho}$ versus $[(\varepsilon_1 - \varepsilon_2)^2/(\varepsilon_1 + \varepsilon_2)]\ (1/\sqrt{\gamma})$ for a monolayer of non-ionic surfactant ($C_{10}E_4$) at the water–octane interface ($\varepsilon_1 = n_1^2$; $\varepsilon_2 = n_2^2$).

Ellipsometry is a simple technique, but the wavelength of the visible light limits its use to large thermal fluctuations, i.e. to monolayers of low surface tension at the oil–water interfaces. X-ray reflectivity is suitable for monolayers at the free surface of water but is less accurate than ellipsometry at small scales.

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