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Liquid interfaces : role of the fluctuations and analysis of ellipsometry and reflectivity measurements

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Résumé. — Nous montrons que les difficultés qui apparaissent dans l'interprétation des propriétés optiques des interfaces liquides disparaissent quand on développe une théorie prenant en compte le couplage entre les modes thermiques de fluctuations de l'interface. Une telle théorie permet de déduire les propriétés optiques des interfaces critiques en ne prenant en compte que des paramètres macroscopiques dont aucun n'est ajustable. Lorsque les interfaces, tels que les monocouches de surfactants, présentent une rigidité, cette théorie permet d'extraire un coefficient de rigidité à toute échelle des mesures d'ellipsométrie. La longueur de persistance déduite de ce coefficient de rigidité est en accord avec les structures de phases observées.

Abstract. — It is shown that the difficulties which appear in the interpretation of optical properties of liquid interfaces disappear when we develop a coupled mode theory of thermal interfacial fluctuations. First, we are able to calculate the optical properties of critical interfaces with only macroscopic non adjustable parameters. Secondly, we can deduce the rigidity constant at any length scale of monolayers from ellipsometric measurements. The persistence lengths of monolayers that we deduce are in perfect agreement with the phase structures we observe.

1. Introduction.

Optical measurements are currently used to get information about planar liquid interfaces. In this paper, we are interested in two of them : ellipsometry and reflectivity measurements. Ellipsometry is the more sensitive one and has been used for a long time [1, 2] while reflectivity measurements were applied more recently to the study of thick liquid interfaces [3-5]. These techniques are sensitive to two features of interfaces : the thickness of a layer (e.g. a surfactant layer) or a possible diffuse layer at liquid vapor interfaces for instance [28-30] in which the refractive index changes from n_1 to n_2 , the indexes of the two superposed phases, and the roughness of interfaces which is due to the thermal motion. So the interpretation of these optical measurements needs to connect the roughness with physical parameters of the interface. Early analysis of ellipsometry measurements took into account only an interfacial thickness [1, 2, 6]. In the same way Webb and collaborators [3, 4] neglected the roughness of

critical interfaces in reflectivity measurements. Later, a new analysis of these reflectivity measurements [5] and of other ones [8] took into account the roughness assuming that thermal fluctuations are a sum of independent capillary waves. But this summation over capillary waves needs the introduction of a cut-off at a microscopic scale to avoid any divergence and the value of this cut-off is not well defined. This is not dramatic in the case of the reflectivity where this cut-off appears in a logarithmic term. The value of the cut-off is very important in ellipsometry and roughness was mentioned but could never be exactly taken into account in the analysis of experimental studies [7-9] except in the case of a surfactant monolayer [10, 11]. In this case a natural cut-off is introduced by the rigidity of the monolayer and ellipsometry is then a good technique to measure this rigidity. However new difficulties appear : on the one hand the approximation of independent surface modes used for this analysis leads to a constant rigidity and it is well-known that the rigidity is a function of the scale of observation [12, 13] ; on

the other hand, the measured rigidity constant is sometimes too large, sometimes too small, to explain some properties of the monolayer [11, 14].

Our purpose is to take into account the coupling of the modes ; then we show that the difficulties mentioned above disappear and we obtain a very good agreement between theory and experiment.

We first give a survey of the state of the problem (Sect. 2). We examine the consequences of the coupling between modes on the behaviour of the surface tension, the rigidity and the persistence length (Sect. 3), then on optical properties of interfaces (4). We show that most of the interfaces can be described as thin but rough interfaces. The measurements at critical interfaces and liquid-air interfaces are compared to the calculated values of this model (Sect. 5). The previously reported ellipsometric measurements [10, 11] on surfactant monolayers at the oil/water interface are investigated again and new values of the rigidity are obtained (Sect. 6).

2. Optical properties of liquid interfaces.

2.1 ELLIPSONOMETRY AND REFLECTIVITY. — A planar liquid interface is more or less rough and thick. In this letter, we shall consider interfaces with thickness and roughness smaller than the wavelength of light (λ). E_j is the electric field of the incident light of polarization j and E'_{ij} is the electric field of the reflected light of polarization i , then :

$$E'_{ij} = r_{ij}(\theta) E_j$$

where θ is the incidence angle and j is equal to p or s according as E_j is parallel or perpendicular to the plane of incidence.

Ellipsometry allows us to measure the ratio $\mu = (r_{ps} + r_{pp}) / (r_{ss} + r_{sp})$. The best sensitivity is obtained at the Brewster angle $\theta = \theta_B$ and we shall only consider this case. At this angle, the real part of $(r_{ps} + r_{pp})$ vanishes and the phase difference between $E_{ps} + E_{pp}$ and $E_{ss} + E_{sp}$ is $\pi/2$; the ratio μ becomes $i\bar{\rho}_B$ where $\bar{\rho}_B$ is the ellipticity, a real number. This quantity may be written as the sum of two contributions :

$$\bar{\rho}_B = \bar{\rho}_B^L + \bar{\rho}_B^R \quad (1)$$

$\bar{\rho}_B^L$ is the contribution of the thickness of the interface $\bar{\rho}_B^R$ is the contribution of the roughness.

The other parameter used in ellipsometry measurement is :

$$\eta = \frac{\lambda}{\pi} \frac{n_1^2 - n_2^2}{\sqrt{n_1^2 + n_2^2}} \bar{\rho}$$

η has the dimension of a length and its value is usually a few Å. We get from (1) :

$$\eta = \eta^L + \eta^R \quad (1')$$

η^L is given by the Drude formula [6] and η^R by [7, 15] :

$$\eta^R = -\frac{3}{2} \frac{(n_1^2 - n_2^2)^2}{(n_1^2 + n_2^2)} \sum_q q \langle \zeta_q^2 \rangle \quad (2)$$

where ζ_q is the amplitude of the mode of wave vector q of the roughness of the interface (the vertical displacement of the interface at the point r at the time t is $\zeta(r, t)$:

$$\zeta = \sum_q \zeta_q \exp iqr.$$

Equation (2) is only valid for $q \gg 2\pi/\lambda$. A very simple demonstration of equation (2) is presented in the appendix A. Although the equation (2) is only valid for $q > 2\pi/\lambda$, numerical calculation of η^R can be made for $q \sim 2\pi/\lambda$ as is also shown in appendix A.

The general expression of the interface reflectivity is :

$$R_i = |r_{ii}|^2 + |r_{ji}|^2.$$

Let us consider a very simple case of normal incidence which leads to $r_{ij}(0) = \delta_{ij}r$ and $R_i = R$; with the assumption that the thickness of the interface is described by an error function, one gets [5] :

$$\begin{aligned} \mathcal{R} = R/R_F &= \exp -4k^2(L_p^2 + \langle \zeta^2 \rangle) \\ &= \exp -4k^2L^2 \end{aligned} \quad (3)$$

where k is the wave number of the light $k = 2\pi/\lambda$; R_F is Fresnel reflectivity, i.e. the reflectivity of an ideal interface without any thickness or roughness :

$$R_F = (n_1 - n_2)^2 / (n_1 + n_2)^2$$

L_p is the thickness of the interface, $\langle \zeta^2 \rangle$ the average of the square amplitude of the roughness :

$$\langle \zeta^2 \rangle = \sum_q \langle \zeta_q^2 \rangle. \quad (4)$$

From equation (3), one sees that one cannot get any information about interfaces such as $(L_p^2 + \langle \zeta^2 \rangle)^{1/2} \leq 100 \text{ \AA}$, i.e. most of free liquid surfaces and monolayers.

It must also be pointed out that the reflectivity is equally sensitive to the different modes ζ_q , whereas ellipsometry is more sensitive to the modes of large q (formulae (2) and (3)).

2.2 THE APPROXIMATION OF INDEPENDENT MODES.

— The first approximation for $\langle \zeta^2 \rangle$ and $\sum_q q \langle \zeta_q^2 \rangle$ is obtained with a model of independent capillary

waves. Then the average of the square amplitude of a mode q excited by thermal motion is :

$$\langle \xi_q^2 \rangle = \frac{k_B T}{\Delta\rho \cdot g + \gamma q^2} \quad (5)$$

where γ is the interfacial tension and $\Delta\rho \cdot g$ the gravity term which avoids the divergence of $\langle \xi_q^2 \rangle$ at small q ($\Delta\rho$ is the density difference between the two phases and $g = 981 \text{ cm/s}^2$). One obtains :

$$\begin{aligned} \langle \xi^2 \rangle &= \frac{k_B T}{4 \pi \gamma} \text{Ln} (\ell_c^2 q_R^2 + 1) \\ &\approx \frac{\ell_m^2}{2 \pi} \text{Ln} (\ell_c q_R) \end{aligned} \quad (6)$$

and :

$$\sum_q q \langle \xi_q^2 \rangle = \frac{k_B T}{2 \pi \gamma} q_e = \frac{\ell_m^2}{2 \pi} q_e \quad (7)$$

$\ell_c = (\gamma/\Delta\rho \cdot g)^{1/2}$ is the capillary length ; q_R and q_e are upper cut-offs for the capillary waves and $\ell_m^2 = K_B T/\gamma$.

Obviously, q_R and $q_e \sim 1/\Lambda$ where Λ is the correlation length ξ' for a critical interface or a molecular length for an interface between two fluids far from a critical point. However this approach gives no exact information about q_e and q_R values which is particularly dramatic in the case of ellipsometry where $\bar{\rho}_B^R$ is directly proportional to q_e (see Eqs. (2) and (7)).

The introduction of the two parameters q_e and q_R is needed to avoid the high q divergences in the summations. The origin of these divergences is the lack of terms of degree higher than 2 in the denominator of (5). In the case of a layer at the interface, it is natural to introduce a curvature energy term Kq^4 :

$$\langle \xi_q^2 \rangle = \frac{k_B T}{\Delta\rho \cdot g + \gamma q^2 + Kq^4} \quad (8)$$

where K , the rigidity of the layer, is constant in the approximation of independent modes. The integration of (8) leads to a new expression of $\langle \xi^2 \rangle$, from which, when compared with equation (6), q_R value is deduced :

$$q_R = \sqrt{\frac{\gamma}{K}}. \quad (9a)$$

In the same way, q_e value is deduced by comparing equation (7) with the integration of $q \langle \xi_q^2 \rangle$ where $\langle \xi_q^2 \rangle$ is given by (8) :

$$q_e = \frac{\pi}{2} \sqrt{\frac{\gamma}{K}}. \quad (9b)$$

Formula (9b) was used to deduce the rigidity constant of surfactant monolayers from ellipsometric measurements [10, 11].

We must however point out that the approximation of independent modes is not fully satisfactory :

— In the case of a critical interface, we expect $K = 0$ and because of the divergence of the integrals used in the above calculation, an heuristic cut-off must be introduced.

— The K experimental values deduced from ellipsometric measurements using (9b) do not agree with the observed structures in a mixture of oil, water and surfactant [11, 14].

— It is well known that for large q the hydrodynamic modes cannot be considered as independent and consequently γ and K are functions of q [12, 13].

In order to overcome these points, in the following we will develop a mode coupling theory.

3. Surface tension, rigidity coefficient and persistence length of an interface with coupled thermal modes.

3.1 SURFACE TENSION AND RIGIDITY. — γ and K respectively are now functions of the length scale $1/q$:

$$\langle \xi_q^2 \rangle = \frac{k_B T}{\Delta\rho \cdot g + \gamma(q) q^2 + K(q) q^4} \quad (10)$$

where $\gamma(q)$ and $K(q)$ are given by (see appendix B) :

$$d\gamma(q) = 2 a k_B T q dq \quad (11)$$

$$dK(q) = 2 a k_B T \left(\frac{K(q)}{\gamma(q) + K(q) q^2} q dq \right) \quad (12)$$

and $a = 3/8 \pi$.

Integration of equation (11) gives :

$$\gamma(q) = \gamma_\infty + a k_B T q^2 \quad (13)$$

where γ_∞ is the macroscopic interfacial tension. $\gamma(q)$ is significantly higher than γ_∞ only for large q ($q \geq 10^6 \text{ cm}^{-1}$). For simplicity, we will distinguish two cases :

— where the macroscopic surface tension vanishes ($\gamma_\infty = 0$).

Integration of equation (12) gives :

$$K(q) = K_1 + a k_B T \text{Log} [q^2 K_1/q_1^2 K(q)] \quad (14)$$

where K_1 is the rigidity observed at a length scale $1/q_1$. By rearrangement of the terms of equation (14), one gets :

$$H(q) = K(q)/(k_B T) = a \text{Log} [A^2 q^2/H(q)]. \quad (14')$$

The variation of $H(Aq)$ with Aq is represented in figure 1. H is always positive and vanishes as $q \rightarrow 0$. This reduction of K with the increasing

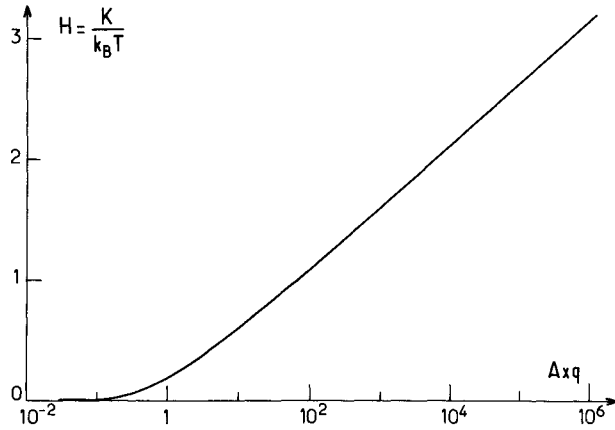


Fig. 1. — The reduced rigidity constant $K/k_B T$ versus Aq for an interface without macroscopic interfacial tension ($\gamma_\infty = 0$). A is a constant and q the wave vector.

observation scale agrees with the result obtained by Peliti and Leibler [13] if we neglect the K variation in the logarithm, i.e. provided we neglect the surface tension term, $ak_B Tq^2$, in equations (12) and (13)

— where the macroscopic surface tension does not vanish :

There are two asymptotic solutions :

(a) for $(K + ak_B T) q^2 \ll \gamma_\infty$, one gets from equation (12) : $K = K_\infty$.

(b) for $(K + ak_B T) q^2 \gg \gamma_\infty$, one gets $K(q)$ which is given by expression (14).

(c) in the intermediate domain

$$(K + ak_B T) q^2 \sim \gamma_\infty$$

using the dimensionless variables :

$$Q = \sqrt{k_B T / \gamma_\infty} q \quad \text{and} \quad H(q) = K(q) / k_B T$$

then equation (12) can be written :

$$dH(Q) = a \frac{H(Q)}{1 + [H(Q) + a] Q^2} 2 Q dQ. \quad (15)$$

Solutions of this equation are given in figure 2. Each solution can be identified with H_∞ , the macroscopic value of H ; but we are interested in the values of H for large Q . A better parameter to characterize a solution is $Z = (\sqrt{H}/Q) \exp H/2a$ for large Q . This parameter is constant for each solution as long as the q^2 term can be neglected. Its value allows us to calculate $H(Q)$ for large Q by solving the equation :

$$ZQ = \sqrt{H} \exp(H/2a) \quad (16)$$

the solution of which is given in figure 3.

3.2 PERSISTENCE LENGTH. — P. G. de Gennes and C. Taupin [16] define the persistence length ξ_K of a monolayer by the following procedure : at the dis-

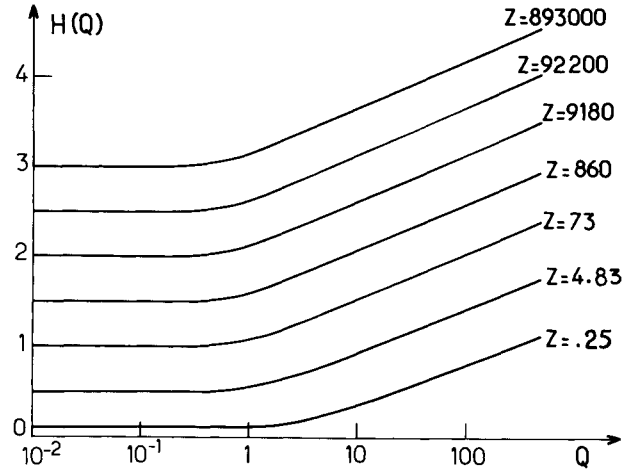


Fig. 2. — Solutions for the reduced rigidity constant H versus the reduced wave vector Q for interfaces with macroscopic interfacial tension $\gamma_\infty \neq 0$. H is a constant when the capillary energy is larger than the curvature energy.

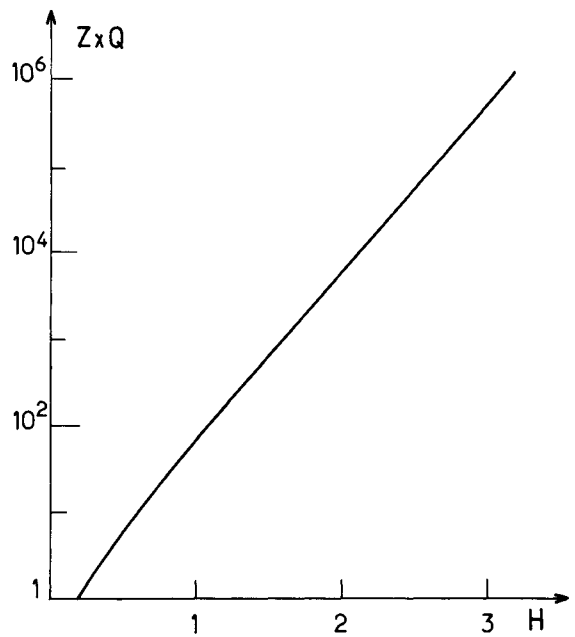


Fig. 3. — $Z \times Q$ versus H . This curve allows us to solve the equation $ZQ = \sqrt{H} \exp(H/2a)$ for given Z and Q .

tance $r = \xi_K$ the angular correlation $\langle \cos \theta(r) \rangle$ of the normals to the interface is $1/e$. They determine ξ_K for a K independent of the scale. Taking into account the q -dependence of K , we obtain the angular correlation :

$$\langle \theta^2(r) \rangle = \frac{1}{\pi} \int_0^{2\pi/\Lambda} [1 - J_0(qr)] \frac{dq}{q[H(q) + a]}$$

Λ is a microscopic length related to the molecular size in the monolayer and J_0 the zero order Bessel

function. The persistence length is useful in the case of monolayer without macroscopic surface tension. Using equation (12) with $\gamma_\infty = 0$, $H = K/k_B T$ and the approximations of reference [16], one gets :

$$\langle \cos \theta \rangle \approx 1 - \frac{2}{3} \text{Log} \frac{H(2 \pi/\Lambda)}{H(2 \pi/r)} \approx \left[\frac{H(2 \pi/r)}{H(2 \pi/\Lambda)} \right]^{2/3}$$

The new expression of the persistence length becomes :

$$H(2 \pi/\xi_K) = H(2 \pi/\Lambda)/e^{1.5} \quad (17)$$

Here ξ_K is the length over which the microscopic rigidity constant is decreased by a factor $e^{1.5}$. Substituting (14') in (17), one gets :

$$\frac{\xi_K}{\Lambda} = \sqrt{S} \exp \left[\frac{S-1}{2S} \frac{H(2 \pi/\Lambda)}{a} \right] \approx 2.117 \exp \{ 3.254 [H(2 \pi/\Lambda) + 0.230] \}$$

where $S = e^{1.5}$.

4. Optical measurements on a rough liquid interface.

Coupled modes theory leads to a q^4 term in the expression of $\langle \xi_q^2 \rangle$, even for $K(q) = 0$. This term introduces a natural cut-off in summations $\Sigma \langle \xi_q^2 \rangle$ and $\Sigma q \langle \xi_q^2 \rangle$. We first examine the case $K = 0$ which is expected for a symmetrical profile of density interfaces (i.e. critical interfaces [17]), then the case $K \neq 0$.

4.1 INTERFACE WITHOUT RIGIDITY. — Substituting (13) in (5), we get a natural cut-off for (6) and (7) :

$$q_R = \frac{Q_R}{\ell_m} \quad \text{with} \quad Q_R = \frac{1}{\sqrt{a}} \quad \text{and} \quad \ell_m = \sqrt{\frac{k_B T}{\gamma_\infty}} \quad (18)$$

and

$$q_c = \frac{Q_c}{\ell_m} \quad \text{with} \quad Q_c = \frac{\pi}{2} \frac{1}{\sqrt{a}} \quad (18')$$

The reflectivity of a thin interface with coupled capillary modes is fully determined by two macroscopic parameters $\Delta\rho$ and γ_∞ , whereas ellipticity is fully determined by one parameter γ_∞ .

It is shown (Sect. 5) that a coupled modes approach is in excellent agreement with experimental data obtained from critical interfaces and no extra thickness is needed to fit experimental values. This point of view must be reconciled with the previous one : a critical interface is a thick interface described by a Fisk and Widom [3] profile of thickness L_p , and thermal fluctuations are considered as independent modes with a cut-off π/L_p . This last point of view was used to analyse reflectivity measurements.

For reflectivity, a thin interface with thermal modes described by coupled modes theory is equivalent to a thin interface with independent modes and a cut-off (Eq. (18)) :

$$q_R = \sqrt{\frac{\gamma_\infty}{ak_B T}}$$

Taking into account the formula [19, 20] :

$$\gamma_\infty = \frac{k_B T}{R\xi^2} \quad (19)$$

(the experimental value for R is ≈ 2.6) where ξ is the correlation length above T_c , we obtain :

$$q_R \approx 1.8/\xi$$

From the other point of view, the roughness of the interface $\langle \xi^2 \rangle$ can be separated into two parts :

$$\langle \xi^2 \rangle = \sum_{q=0}^{q_{\max}} \langle \xi_q^2 \rangle + \sum_{q_{\max}}^{\infty} \langle \xi_q^2 \rangle \quad (20)$$

where q_{\max} is a cut-off ($q_{\max} < q_R$). The second part :

$$L_p^2 = \sum_{q_{\max}}^{\infty} \langle \xi_q^2 \rangle$$

can be interpreted as a diffuse layer with a profile described by an error function [3, 5, 20] :

$$\rho(z) = \frac{1}{2} \left\{ (\rho_1 + \rho_2) + \frac{2}{\sqrt{\pi}} \Delta\rho \times \int_0^{z/\sqrt{2}L_p} e^{-t^2} dt \right\} \quad (21)$$

where L_p is the thickness of the layer.

The shape of this profile is very close to the Fisk and Widom one [3]. By the choice of q_{\max} , it is possible to adjust L_p^2 to the value expected by the Fisk and Widom theory [20] :

$$L_p \approx \frac{2 \xi}{\sqrt{2 \pi}}$$

and

$$L_p^2 = \frac{k_B T}{4 \pi \gamma_\infty} \text{Ln} \frac{1.8}{\xi \cdot q_{\max}}$$

Taking into account equation (19) :

$$q_{\max} \approx \frac{1}{2.55 \xi} \quad (22)$$

This value of the cut-off agrees with the one used in reference [5].

Recently, Beyssens and Robert [20] reanalyse the

experimental results using a « bare » surface tension [18] for the capillary waves :

$$\gamma_0 = \gamma_\infty + \frac{3}{16\pi} k_B T q_{\max}^2.$$

The value of r in their cut-off $q_{\max} = \pi/r\xi$ is found to be 4 or 5, a value smaller than the one in formula (22) because γ_0 is higher than γ_∞ .

In conclusion, there are two equivalent points of view for the reflectivity of the interface :

— the interface is thick and is described by the Van der Waals or Fisk and Widom density profile. This description is only valid for fluctuations at small scale and capillary waves must be introduced at large scale with an empirical cut-off q_{\max} ;

— the interface is thin but rough. The origin of the roughness is capillary waves. The coupling between these waves introduces a natural cut-off.

This description is equivalent to the previous one, but needs no empirical cut-off for high q wave vectors.

4.2 INTERFACES WITH RIGIDITY.— Let us now consider a thin interface with rigidity and coupled thermal modes. The cut-off Q_c and Q_R are then given by :

$$Q_c = \int_0^\infty \frac{dQ}{1 + (H+a)Q^2} \quad (23)$$

where H is a solution of equation (15). Numerical values for Q_c versus Z are given in figure 4. Q_R is a function of two parameters : ℓ_m/ℓ_c and Z :

$$Q_R = \frac{\ell_m}{\ell_c} \exp \int_0^\infty \frac{2Q dQ}{(\ell_m/\ell_c)^2 + Q^2 + (H+a)Q^4}. \quad (24)$$

In practice $\ell_m^2/\ell_c^2 \leq 10^{-5}$ and $H+a \sim 1$. Thus the above summation can be separated into two parts :

$$Q_R = \frac{\ell_m}{\ell_c} \left[10^{-1} \frac{\ell_c}{\ell_m} + A' \right] \quad (25)$$

where

$$A' = \int_{0.1}^\infty \frac{dQ/Q}{1 + (H+a)Q^2}$$

A' is only a function of Z and is given in figure 4. Because there is a monolayer at the rigid interfaces studied in section 5, the measured ellipsometric parameter is $\eta = \eta^L + \eta^R$. η^L can be determined independently and from η^R , we can deduce the cut-off Q_c (Eqs. (2) and (7)) and then the parameter Z (Eq. (23) or Fig. 4) which gives us the value of the rigidity versus the scale of length (Fig. 2).

Although the same analysis can be done with reflectivity measurements (Eq. (25)), this technique is not sensitive enough to get accurate values for Z .

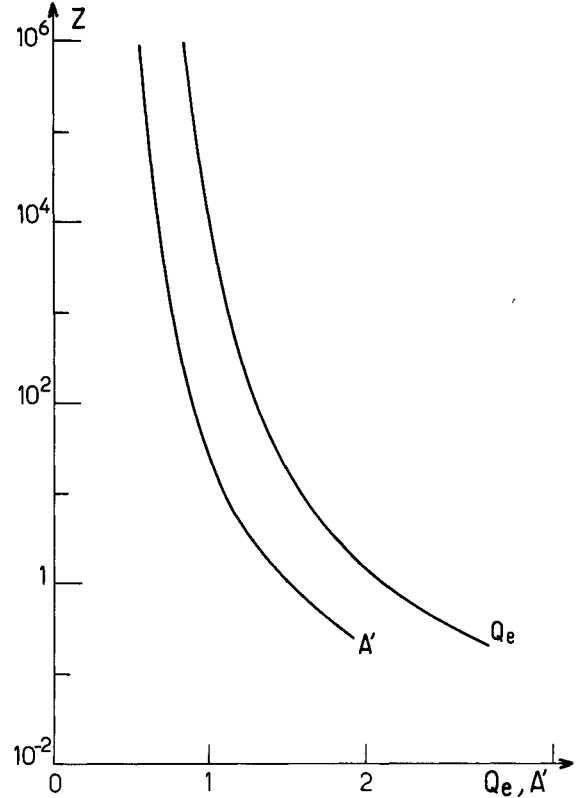


Fig. 4. — The reduced cut-off Q_c and A' versus Z .

5. Analysis of optical measurements at critical interfaces and at liquid-air interfaces.

The surface tension of a critical interface vanishes at the critical temperature $T = T_c$:

$$\gamma_\infty \sim \Delta T^\mu \quad \text{with} \quad \Delta T = T_c - T$$

$$\mu \approx 1.30.$$

So, the roughness of a critical interface is large and easily observable not only by ellipsometry but also by reflectivity. In these interfaces, the density profile is symmetrical and that's why the rigidity constant must vanish [17] ($K = 0$). In this section, we compare the available measurements with the calculated values in our model for a thin interface with coupled capillary waves (Sect. 3.1). The best test for this model is ellipsometry because η is very sensitive to the cut-off Q_c ($\eta^R \sim Q_c$).

Liquid-air interfaces have no reason to have a symmetrical density profile ($K \neq 0$) ; nevertheless because the K value is expected to be low, the approximation $K \approx 0$ seems reasonable, that's why in section 5.2 we shall compare experimental values with the theoretical estimations of our model with $K = 0$.

5.1 CRITICAL INTERFACES. — *Ellipsometry* : to our knowledge, the only experimental results are due to Beaglehole [7, 8] and concern argon liquid-vapor

interfaces and critical interfaces of a cyclohexane-methanol mixture.

The measurements at the liquid-vapor interface of argon are performed far from the critical point T_c ($31^\circ < \Delta T = T_c - T < 66^\circ \text{C}$) because it is difficult to have windows free of strain in a high pressure cell.

The experimental values $\bar{\rho}_B^m$ and the calculated ones $\bar{\rho}_B^R$ are given in tables I and II. In the two cases, the difference between these two values is small (smaller than 15 % in the first case and 6 % in the second one) and can be explained by the experimental uncertainties in γ , ε_1 and ε_2 , $\bar{\rho}_B^m$.

— *Reflectivity*: two critical interfaces were studied with this technique [3, 4]. These measurements include part of the scattered light in their specular reflectivity measurements. The data analysis can be done simply using equation (3) with $L_p = 0$ but replacing $\langle \xi^2 \rangle$ by $\langle \xi'^2 \rangle$, where $\langle \xi'^2 \rangle$ represents the contribution of the wave vectors $q > q_{\min}$, and $q_{\min} = k \sin \theta$, 2θ being the collection angle. In this way, the contribution of the wave vectors $0 < q < q_{\min}$ that scatter light into the aperture used to collect the specular reflection is subtracted. So we must put $1/q_{\min}^2$ in place of ℓ_c^2 in equation (6).

The experimental data for L (Eq. (3)) are reported

in tables III and IV and compared with the calculated values $\langle \xi'^2 \rangle^{1/2}$ for three values of θ : 0 ; 0.005 and 0.01 (the instrumental value of θ is not known exactly). A good agreement between experimental values of L and calculated ones is obtained for the liquid-vapor interface of SF_6 (Tab. III) but there is a large discrepancy for the critical interface in a cyclohexane-methanol mixture (Tab. IV). Much better agreement with experimental values is obtained when additional thickness $L_p \sim \langle \xi'^2 \rangle^{1/2}$ is introduced.

Recently, Beysens [20] noticed that the interfacial tensions measured at this last interface [26] do not agree with formula (19). This discrepancy seems to be explained by an error in the measurement of interfacial tension in reference [26]. Thus he proposed to deduce γ_∞ from (19) with :

$$\xi = 3.24 \left[\frac{\Delta T}{T_c} \right]^{-0.630} \text{ reference [21]}$$

we obtain :

$$\gamma_\infty = 1.08 (\Delta T)^{1.260} .$$

With this estimated value of γ , the agreement between the measured and the calculated reflectivity is good (Tab. IV).

Table I. — *The measured ellipticity $\bar{\rho}_B^m$ of the reflected light at Brewster angle on liquid-vapor argon versus the temperature [7] and the calculated ellipticity $\bar{\rho}_B^R$ for a thin interface with the same macroscopic interfacial tension γ_∞ . The critical temperature of argon is $T_c = 150.9^\circ \text{K}$. ε_1 , ε_2 , γ_∞ are experimental values [7]. The wavelength of the light was $\lambda = 6328 \text{ \AA}$.*

T ($^\circ \text{K}$)	$\varepsilon_1 - \varepsilon_2$	$\varepsilon_1 + \varepsilon_2$	γ_∞	$\bar{\rho}_B^R$	$\bar{\rho}_B^m$
85	0.5132	2.5162	13.2	4.87	5.4 ± 0.4
90	0.5001	2.5051	11.86	5.43	5.7 ± 0.4
100	0.4694	2.4806	9.42	6.06	6.5 ± 0.4
110	0.4147	2.4553	7.10	6.5	7.5 ± 0.4
120	0.3954	2.4320	4.95	7.8	8.8 ± 0.6

Table II. — *The measured ellipticity $\bar{\rho}_B^m$ of the reflected light at Brewster angle on the critical interface of a cyclohexane-aniline mixture versus the temperature and the calculated one $\bar{\rho}_B^R$ for a thin interface with the same macroscopic interfacial tension γ_∞ . The critical temperature of the mixture is $T_c = 29.6^\circ \text{C}$ and the wavelength of the light $\lambda = 6328 \text{ \AA}$.*

		Temperature range	Ref.
Surface tension	$\gamma_\infty = 0.0225 \Delta T^{1.48}$	$0.35 < \Delta T < 3.2^\circ$	[23]
Dielectric constants	$\varepsilon_1 - \varepsilon_2 = 0.128 \Delta T^{0.34}$ $\varepsilon_1 + \varepsilon_2 = 4.4$		[8] [8]
Calculated ellipticity	$\bar{\rho}_B^R = (4.39 \times 10^{-3}) \Delta T^{-0.4}$		
Measured ellipticity	$\bar{\rho}_B^m = (4.28 \times 10^{-3}) \Delta T^{-0.375}$	$0.3 < \Delta T < 5^\circ$	[8]

Table III. — *Liquid-vapor critical interface of SF₆. The « thickness » L of the interface deduced from reflectivity measurements and the one $\langle \zeta'^2 \rangle^{1/2}$ calculated for a thin but rough interface of same macroscopic interfacial tension and for three collection angle θ . The critical temperature is $T_c = 45.53$ °C, the wavelength of the light 4 579 Å. We must remark that the value L of reference [4] is divided by $\sqrt{2 \pi}$ to agree with formula (3).*

			Temperature range	Ref.
$\Delta\rho$		$(0.496 \pm 15) \Delta T^{0.339 \pm 0.006}$		[25]
γ_∞		$(3.34 \pm 16) 10^{-2} \Delta T^{-1.285 \pm 0.016}$	$0.03 < \Delta T < 25$ °C	[24]
L (Å)		$(148 \pm 9) \Delta T^{-0.62 \pm 0.01}$	$0.03 < \Delta T < 20$ °C	[4]
$\langle \zeta'^2 \rangle^{1/2}$ (Å)	$\theta = 0$	$(144 \pm 7) \Delta T^{-0.573 \pm 0.02}$		
	$\theta = 5 \times 10^{-3}$	$(132 \pm 7) \Delta T^{-0.587 \pm 0.02}$		
	$\theta = 10^{-2}$	$(126 \pm 6.5) \Delta T^{-0.59 \pm 0.02}$		

Table IV. — *Critical interface of a cyclohexane-methanol mixture. The « thickness » L of the interface deduced from reflectivity measurements and the calculated one for different collection angles θ and for two γ_∞ values. The first one is experimental, the second one is deduced from the correlation length (see Sect. 5.1). We must remark that the value L of reference [3] is divided by $\sqrt{2 \pi}$ to agree with formula (3). The wavelength of the light is 6 328 Å.*

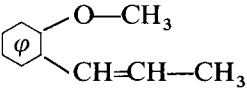
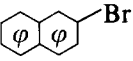

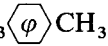
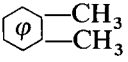
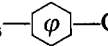
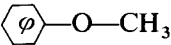
			Temperature range	Ref.
$\Delta\rho$		$(0.0026 \pm 0.0003) \Delta T^{0.34 \pm 0.02}$		[26]
γ_∞		$(0.08 \pm 0.02) \Delta T^{1.23}$	$0.1 < \Delta T < 10$ °C	[26]
L (Å)		$(186 \pm 6) \Delta T^{-0.665 \pm 0.01}$	$0.02 < \Delta T < 3$ °C	[3]
$\langle \zeta'^2 \rangle^{1/2}$ (Å)	$\theta = 0$	$(108 \pm 28) \Delta T^{-0.565}$		
	$\theta = 5 \times 10^{-3}$	$(88.6 \pm 22) \Delta T^{-0.568}$		
	$\theta = 10^{-2}$	$(85 \pm 22) \Delta T^{-0.568}$		
γ_∞		$0.0108 \Delta T^{1.260}$		[20, 21]
$\langle \zeta'^2 \rangle^{1/2}$	$\theta = 10^{-2}$	$(215 \pm 20) \Delta T^{-0.0580}$		

In conclusion, by considering the coupled mode model, the hypothesis of diffuse layers is no longer necessary to fit experimental results and only two macroscopic parameters are needed to describe the behaviour of critical interfaces. This conclusion seems to be at variance with that of a recent paper [27] in which the author claimed to distinguish between a diffuse (Fisk-Widom) contribution to the interfacial thickness near the critical point and surface waves far from the critical point. In fact, the conclusion of this author is based upon the use of scaling laws in a large temperature range ($T_c/2 <$

$T < T_c$) where there is no reason for them to remain valid.

5.2 LIQUID-AIR INTERFACES. — Since the end of the last century, a large number of experimental results have become available. However, well controlled clean interfaces are difficult to obtain, and very large discrepancies in the experimental values (for the same liquids) are reported in the literature. Because of the care reported in his experiments, we feel confident with the experimental values of Bouhet [2] (Tab. V). As expected for interfaces with

Table V. — The measured ellipticity $[2]\bar{\rho}_B^m$ and the calculated one $\bar{\rho}_B^R$ for a thin interface of same macroscopic surface tension with coupled capillary waves and no rigidity. Λ is the intermolecular length and $\lambda = 5\,460 \text{ \AA}$.

	T (°C)	n	γ_∞	Λ (Å)	$2\pi/q_c$	$\bar{\rho}_B^R \times 10^5$	$\bar{\rho}_B^m \times 10^5$	$\frac{\bar{\rho}_B^R - \bar{\rho}_B^m}{\bar{\rho}_B^R}$
	22	1.5633	35.7	6.29	4.62	159	163	- 2.5 %
	17.5	1.6680	44.6	6.11	4.14	168	139	+ 17 %
CHBr ₃	19	1.6025	41.5	5.25	4.29	157	138	+ 12 %
	13	1.5089	29.8	5.29	5.06	158	132	+ 16 %
CH ₃  CH ₃	14.6	1.5026	29	5.90	5.13	158	129	+ 18 %
	17	1.5115	29.3	5.86	5.10	164	127	+ 23 %
CCl ₄	12.5	1.4681	26.9	5.43	5.32	153	126	+ 18 %
C ₉ H ₇ N	12.5	1.6373	44.8	5.81	4.13	160	125.5	+ 22 %
CH ₃  CH ₃	18.7	1.5023	29.1	5.89	5.12	158	123.5	+ 22 %
C ₆ H ₁₂	16.5	1.4295	27.0	5.64	5.31	141	121	+ 14 %
	21.7	1.5207	35	5.65	4.67	149	118.5	+ 20 %
C ₆ H ₅ -CH=CH-CO ₂ -C ₂ H ₅	21.5	1.5554	37.3	6.51	4.52	154	114.5	+ 26 %
CH ₂ Br-CH ₂ Br	17.6	1.5443	38.4	5.22	4.46	148	114.5	23 %
C ₆ H ₅ -CO ₂ -CH ₂ -C ₆ H ₅	21.5	1.5742	43	6.81	4.21	148	109	26 %
CH ₃ -(CH ₂) ₆ -CH ₂ OH	17.7	1.4256	27.7	6.39	5.25	133	102	23 %
CH ₃ -CO ₂ -C ₂ H ₅	15.9	1.3757	24.8	5.86	5.55	129	99	23 %
C ₆ H ₅ -CO ₂ -C ₂ H ₅	16.2	1.5112	35.4	6.20	4.65	145	98	36 %
CH ₃ -CH ₂ OH	16	1.3625	22.6	4.59	5.81	130	92.5	33 %
CH ₃ -(CH ₂) ₇ -CH=CH-(CH ₂) ₇ -CO ₂ H	14.9	1.4653	32.5	8.05	4.84	138	91.5	34 %
CH ₃ -CO ₂ H	21.5	1.3737	27.5	4.57	5.27	121	91	25 %
CO ₂ C ₂ H ₅ -CO ₂ -C ₂ H ₅	22.5	1.4113	32.5	5.59	4.85	123	86.5	30 %
C ₆ H ₅ NO ₂	16.7	1.5614	43.9	5.54	4.17	143	76	47 %
CH ₂ OH-CHOH-CH ₂ OH	15	1.4733	66	4.95	3.4	99	64	33 %
H ₂ O	14.5	1.3345	73.7	3.20	3.2	67	40	40 %

$K \neq 0$, the experimental ellipticity $\bar{\rho}_B^m$ is found inferior or equal to the calculated one; $\bar{\rho}_B^R$ (see Eqs. (2) and (10)). The discrepancy between the experimental values and the calculated ones is less than 25 % for 18 liquid-air interfaces in table V and larger for 6 other ones. This indicates that for all liquid surfaces considered in table V, $K \ll k_B T$.

Let us recall that the summation over the modes q includes q larger than π/Λ (Λ the intermolecular length). This is because in a liquid the molecules are randomly distributed, thus we have no high cut-off at π/Λ as in a lattice. Nevertheless if we introduce a cut-off π/Λ , we must substitute :

$$q'_c = \sqrt{\frac{\gamma_\infty}{ak_B T}} \operatorname{Arctg} \frac{\pi}{\Lambda} \sqrt{\frac{ak_B T}{\gamma_\infty}}$$

for q_c in equation (7). In this case, the new value of $\bar{\rho}_B^R$ deduced from the theory is approximately half the experimental value $\bar{\rho}_B^m$. (The molecular length Λ used here is $\Lambda = (M/\rho N)^{1/3}$ where M is the molecular weight and N the Avogadro number.)

6. Monolayers at the oil-water interfaces.

Recently we measured the ellipticity of light at the oil-water interface covered with a surfactant monolayer [10, 11]. The rigidity coefficient K of the monolayer was deduced from η^R using equations (2), (7) and (9b). η^R was obtained by subtraction of the contribution η^L of the monolayer to η . The rigidity deduced is approximately the rigidity K_c at the length of scale $\Lambda = 1/q_c$. It is a rigidity coefficient measured in the intermediate region ($Kq^2 \sim \gamma$) and it is affected by the interfacial tension. The theoretical model presented above allows us to deduce the rigidity coefficient K for any q (or the parameter Z) from experimental values Q_c as indicated in section 4.2.

The purpose of these K measurements is to explain the microscopic structures of oil-water-surfactant mixtures (bicontinuous phases, birefringent phases...). In these mixtures, we have the same surfactant monolayers as those studied by ellipsometry at the oil-water interface, but the thermal fluctuations of these layers in bulk are such that the interfacial tension γ_∞ vanishes and $K(q)$ is only determined by Z . In particular, we can deduce the persistence length ξ_K of the monolayer (Sect. 3.3). If the spontaneous curvature vanishes, the structure of the phase is given by the value of ξ_K . For $\xi_K \sim 100 \text{ \AA}$, we expect a bicontinuous phase and for larger ξ_K , birefringent phases.

Two monolayers were studied ; but in this paper we shall only examine one case : an SDS-butanol monolayer at the toluene-brine interface at 20°C [10]. The spontaneous curvature C_0 of this layer vanishes for the optimal salinity $S \sim 6.8 \%$. The

ellipsometric measurements were performed in the salinity range (3 %-10 %).

We have deduced from these measurements the rigidity coefficient H at a molecular scale ($q = 2 \times 10^7$ corresponding to a molecular length $\Lambda \approx 5 \text{ \AA}$) : figure 5.

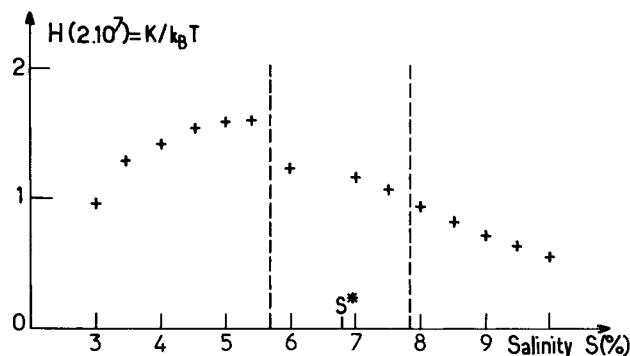


Fig. 5. — The reduced rigidity constant H for $q = 2 \times 10^7$ (a molecular scale) versus the salinity, deduced from ellipsometric measurements at the brine-toluene interface covered with a monolayer of SDS and butanol.

In this case (SDS-butanol monolayer, Fig. 5), the reduced rigidity coefficient H in the vicinity of optimal salinity $S \sim 6.8 \%$ is 1.1 and $\xi_K/\Lambda \approx 70$. The persistence length ξ_K in the vicinity of this salinity is found to be $\xi_K \approx 350 \text{ \AA}$ leading to bicontinuous phases as expected.

7. Conclusion.

We have pointed out the origin of the difficulties of analysis of the optical measurements on liquid interfaces. To solve these difficulties, we have developed a coupled mode theory of interfacial thermal fluctuations. We found for the surface tension a q^2 variation at large q wave vectors and a logarithmic increase of the rigidity K with q , at large q , as expected. At small q , the rigidity keeps a positive value, even for interfaces where the surface tension vanishes (in this case $K = 0$ for small q).

The part of the optical properties of liquid interfaces due to thermal fluctuations has been deduced from this theory.

Comparing optical measurements at critical interfaces, in which the rigidity vanishes, with the calculated values expected from this theory, we have shown that no additional thickness is needed. The advantage of this theory is that one needs only macroscopic parameters — directly measurable — of the interface to explain the optical measurements whereas the previous theory needed an adjustable parameter : a cut-off for capillary waves.

The rigidity constant of surfactant monolayers at oil/water interfaces can be studied *via* ellipsometric measurements. The value of K we deduce with this

theory from experimental results allows us to calculate a persistence length ξ_K of the monolayer, in perfect agreement with the bulk structure in a mixture oil, water and surfactant.

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Appendix A.

The reflectivity coefficients $r_{ps}, r_{pp}, r_{ss}, r_{sp}$ have been calculated at the second order in ζ_q for a thin and plane interface with a sinusoidal deformation of amplitude h_q and wave vector \mathbf{q} (p. 136-137, ref. [22]). At the Brewster angle θ_B and for $q\lambda \gg 1$ formulae (20) and (21) in reference [22] become.

$$r_{1pp} \approx i \pi^2 h_q^2 \frac{n_2^2 - n_1^2}{n_1^2 + n_2^2} \times (n_1 \cos \theta_B - n_2 \sin \theta_B)(1 + \cos^2 \varphi) \frac{q}{\lambda}$$

where φ is the angle of \mathbf{q} with the plane of incidence ($0 < \varphi < \pi$) and $\cotg \theta_B = n_1/n_2$

$$r_{1ps} \approx 0$$

$$r_{1ss} + r_{1sp} \approx r_{1s} = \frac{n_2^2 - n_1^2}{n_1^2 + n_2^2}$$

We obtain :

$$\bar{\rho}_B^R = i \frac{3}{8} \frac{1}{\lambda} \frac{n_1^2 - n_2^2}{\sqrt{n_1^2 + n_2^2}} \int_0^\infty \bar{h}_q^2 q dq$$

h_q is the amplitude of a roughness of $2\pi/q$

wavelength: $h_q^2 = 2 \zeta_q \zeta_q^*$, and we obtain formula (2).

This derivation needs $q \gg 2\pi/\lambda$. In the case $q \sim 2\pi/\lambda$, we can easily obtain $\bar{\rho}_B^R$ by a numerical integration of formula (20) in reference [22].

Appendix B.

The energy of a layer is the sum of the capillary energy and the curvature elastic energy. Two terms contribute to the elastic energy. The origin of the first one is the Gaussian curvature of the layer and is a constant for small fluctuations of a well defined layer because it depends only on the genus of this layer. The origin of the second one is the mean curvature $C = 1/R_1 + 1/R_2$ where R_1 and R_2 are the curvature radii of the layer

$$E = \int dS \left[\gamma'_0 + \frac{K_0}{2} (C - C_0)^2 \right]$$

γ'_0 is the capillary constant and K_0 is the rigidity constant associated with the mean curvature. The layers we consider are flat at equilibrium but thermal motion constantly distorts the surface and gives rise to a certain roughness. The summation over the linear term in C vanishes and the energy of a layer is :

$$E = \int dS \left[\left(\gamma'_0 + \frac{K_0}{2} C_0^2 \right) + \frac{K_0}{2} C^2 \right]$$

with

$$dS = \sqrt{1 + (\nabla \zeta)^2} dx dy ;$$

$$C = \text{div} \frac{\nabla \zeta}{\sqrt{1 + (\nabla \zeta)^2}} .$$

The surface tension effectively measured at the interface is :

$$\gamma_0 = \gamma'_0 + \frac{K_0}{2} C_0^2 .$$

For small fluctuations :

$$dS = \left\{ 1 + \frac{1}{2} (\nabla \zeta)^2 - \frac{1}{8} [(\nabla \zeta)^2]^2 + \dots \right\} dx dy$$

$$C^2 = \left\{ (\Delta \zeta)^2 - (\nabla \zeta)^2 (\Delta \zeta)^2 - 2 \left[\left(\frac{\partial \zeta}{\partial x} \right)^2 \frac{\partial^2 \zeta}{\partial x^2} + \left(\frac{\partial \zeta}{\partial y} \right)^2 \frac{\partial^2 \zeta}{\partial y^2} + 2 \frac{\partial \zeta}{\partial x} \frac{\partial \zeta}{\partial y} \frac{\partial^2 \zeta}{\partial x \partial y} \right] \left[\frac{\partial^2 \zeta}{\partial x^2} + \frac{\partial^2 \zeta}{\partial y^2} \right] + \dots \right\} .$$

The interface is isotropic so $\bar{q}_x^2 = \bar{q}_y^2 = q^2/2$. The average of the term

$$2 \left[\left(\frac{\partial \zeta}{\partial x} \right)^2 \frac{\partial^2 \zeta}{\partial x^2} + \left(\frac{\partial \zeta}{\partial y} \right)^2 \frac{\partial^2 \zeta}{\partial y^2} \right] \left[\frac{\partial^2 \zeta}{\partial x^2} + \frac{\partial^2 \zeta}{\partial y^2} \right]$$

is equivalent to that of $(\nabla \zeta)^2 (\Delta \zeta)^2$; the average of the term

$$\frac{\partial \zeta}{\partial x} \frac{\partial \zeta}{\partial y} \frac{\partial^2 \zeta}{\partial x \partial y} \left[\frac{\partial^2 \zeta}{\partial x^2} + \frac{\partial^2 \zeta}{\partial y^2} \right]$$

vanishes and it can be omitted ; therefore

$$C^2 dS = \left\{ (\Delta\xi)^2 - \frac{3}{2} (\nabla\xi)^2 (\Delta\xi)^2 + \dots \right\}$$

$$E = \int dx dy \left\{ \gamma_0 + \frac{1}{2} [\gamma_0 (\nabla\xi)^2 + K_0 (\Delta\xi)^2]^2 - \frac{3 K_0}{4} (\nabla\xi)^2 (\Delta\xi)^2 + \dots \right\}.$$

The first approximation is given by the quadratic terms. The probability of a fluctuation in this approximation is given by (the average of a term like $\xi_q \xi_{q'}$ vanishes if $q' \neq -q$):

$$\exp - \frac{1}{2 k_B T} \int [\gamma_0 (\nabla\xi)^2 + K_0 (\nabla\xi)^2] dx dy =$$

$$= \prod_q \exp - \frac{S}{2 k_B T} (\gamma_0 q^2 + K_0 q^4) |\xi_q|^2$$

and the fluctuations are independent, the mean square amplitude of which is given by :

$$\frac{k_B T}{\gamma_0 q^2 + K_0 q^4}.$$

The next approximation takes into account the coupling of the modes by terms up to ξ^4 . ξ is the sum of fluctuations of \mathbf{q} wave vector : $\mathbf{q}_0, \mathbf{q}_1, \dots$ and we will suppose $q_0 > q_1 > q_2, \dots$. The spatial average of a term like $\xi_q \xi_{q'} \xi_{q''}$ vanishes and that of a term like $\xi_q \xi_{q'} \xi_{q''} \xi_{q'''}$ vanishes also, except for $\xi_q \xi_{-q} \xi_{q'} \xi_{-q'}$. The Boltzmann factor up to ξ^4 is :

$$\prod_q \exp \frac{S}{k_B T} |\xi_q|^2 \times$$

$$\times \left\{ q^2 \left[\gamma_0 - 3 \sum_{q' > q} (\gamma_0 q'^2 + K_0 q'^4) |\xi_{q'}|^2 \right] + q^4 K_0 \left[1 - 3 \sum_{q' > q} q'^2 |\xi_{q'}|^2 \right] \right\}$$

$$\exp \left\{ - \frac{S}{k_B T} |\xi_{q_1}|^2 \left[q_1^2 \left(\gamma_0 - 3 \sum_{q_0} \frac{k_B T}{S} \right) - q_1^4 \left(K_0 - \frac{3 k_B T}{S} \sum_{q_0} \frac{q_0^2 K_0}{(\gamma_0 q_0^2 + K_0 q_0^4)} \right) \right] \right\}.$$

The mode q_1 appears as an independent mode with a different surface tension γ_1 and a different rigidity constant K_1 . γ_1 is the coefficient of q_1^2 and K_1 the coefficient of q_1^4 .

$$\gamma_1 = \gamma_0 - \frac{3}{2} \sum_{q_0} \frac{k_B T}{S}$$

$$K_1 = K_0 - \frac{3}{2} \sum_{q_0} \frac{k_B T}{S} \frac{q_0^2 K_0}{(\gamma_0 q_0^2 + K_0 q_0^4)}.$$

These relations give the surface tension γ_1 and the

Each quadratic term $|\xi_q^2| |\xi_{q'}^2|$ is much smaller than each squared term $|\xi_q|^4$, but there are many more quadratic terms than square terms, so they have to be taken into account, but the number of terms ξ_q^4 is of the same order of magnitude as the number of square terms, and we can neglect them. The probability that a mode q has an amplitude ξ_q is a function of all the modes $q' > q$. The only independent modes are those of wave vector \mathbf{q}_0 (the highest q), the probability of a mode q_0 is proportional to :

$$\exp - \frac{S}{k_B T} |\xi_{q_0}|^2 (\gamma_0 q_0^2 + K_0 q_0^4).$$

The mean square amplitude of a mode q_0 is that of a free mode :

$$\langle |\xi_{q_0}|^2 \rangle = \frac{k_B T}{2(\gamma_0 q_0^2 + K_0 q_0^4) S}.$$

The probability of a mode q_1 is a function of the modes q_0 and is proportional to :

$$\exp - \frac{S}{k_B T} |\xi_{q_1}|^2 \times$$

$$\times \left\{ q_1^2 \left[\gamma_0 - 3 \sum_{q_0} (\gamma_0 q_0^2 + K_0 q_0^4) |\xi_{q_0}|^2 \right] + q_1^4 K_0 \left[1 - 3 \sum_{q_0} q_0^2 |\xi_{q_0}|^2 \right] \right\}$$

The probability of a mode q_1 , when we take into account all the possible thermal excitation of the mode q_0 , by making an overall average of ξ_{q_0} , is proportional to (using $\langle e^{-A} \rangle \simeq e^{-\langle A \rangle}$):

rigidity constant K_1 observed on a scale of length $1/q_1$ when γ_0 and K_0 are observed on a scale of length $1/q_0$. Assuming the possible values of q are continuous :

$$d\gamma(q) = \frac{3}{4\pi} k_B T q dq$$

$$dK(q) = \frac{3}{4\pi} k_B T \frac{K(q)}{\gamma(q) + K(q) q^2} q dq$$

where $\gamma(q)$ and $K(q)$ are the surface tension and the rigidity constant observed on a scale of length $1/q$.

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