

Surface and Interface Roughness of a Binary-Liquid System

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An extended capillary wave model for a binary-liquid system is developed, which accounts for the coupling between the surface and interface fluctuations due to finite liquid depths. The dispersion relation for a binary-liquid system (a function of wave vector k , liquid depths, densities, and surface and interface tensions) yields two fundamental modes. In a calculation of the mean square roughness, a high- k cutoff is needed to account for nonlinear terms in the Navier-Stokes equation. A low- k cutoff is also needed to correct for a "slip" at the interface due to the neglect of viscosity. The narrowing of the k region is so significant that the mode causing the slip is strongly suppressed, especially if the top film is thin. As a consequence, the calculated interface roughness is significantly smaller than that derived by applying the ordinary one-liquid capillary wave theory to the liquid-liquid interface. Our neutron reflectometry measurements on an oil-water-surfactant system are consistent with this model.

KEYWORDS: capillary waves, liquid-liquid interface, neutron reflectometry

1. Introduction

The theory of capillary waves at an air-liquid interface is often used to describe also the interface between two immiscible liquids, where the lighter one floats on top of the heavier one.¹⁾ Here we discuss the question of applicability of this theory in practical experimental situations where both liquids are not infinitely extended, but are in the form of thin films. For example, in a measurement of the liquid-liquid interface by neutron reflectometry, the use of a thin top film is necessary to reduce the intensity loss due to the scattering in the top liquid phase. Specifically, we ask to what extent the presence of the free surface of the top liquid affects the characteristics of the capillary waves at the liquid-liquid interface, especially in those quite typical cases where the surface tension is large and the interfacial tension is low (as for an oil-water-surfactant system,²⁾ so that a suppression of interface fluctuation due to the "stiff" surface can be expected. We present a detailed calculation of the surface and interface roughness for a binary-liquid system with arbitrary liquid depths. The results are compared to a measurement on the interface roughness of an oil-water-surfactant system using neutron reflectometry. The analysis is an extension of our previous work.³⁾

2. Dispersion relation for a binary-liquid system

The main result of ref. 3 is the dispersion relation for irrotational, capillary modes of a binary-liquid system

$$\omega_{\pm}^2(k) = \left(\frac{(\Omega + \beta^+) + (\Omega - \beta^-)e^{-2kh'} \pm \sqrt{D}}{2(\beta^+ + \beta^-e^{-2kh'})} \right) \omega_0^2 \quad (1)$$

where $D = (\beta^- + \Omega)^2 e^{-4kh'} + 2\{\Omega^2 + 3\Omega(\beta^+ - \beta^-) - \beta^+ \beta^-\} e^{-2kh'} + (\beta^+ - \Omega)^2$ and $\Omega = \omega_0^2 / \omega_0'^2$ with $\omega_0'^2 = gk + \alpha'k^3/\rho'$ and $\omega_0^2 = gk + \alpha k^3/\Delta\rho$. Here, $\omega_{\pm}(k)$ are the frequencies of the two possible modes for a given wave number k , g is the gravitational acceleration, α and α' are the liquid-liquid interfacial tension and air-liquid surface tension, and ρ and ρ' are the bottom and top film density, respectively. $\Delta\rho = \rho - \rho'$ is the density difference, and h and

h' are the thicknesses of the bottom and top liquids, respectively. β^+ and β^- stand for $\beta^+ = (\rho \coth(kh) + \rho')/\Delta\rho$ and $\beta^- = (\rho \coth(kh) - \rho')/\Delta\rho$. The dispersion relation (1) was derived for small wave-like perturbations described by velocities $\mathbf{v} = \nabla\phi$ and $\mathbf{v}' = \nabla\phi'$ which are determined by the velocity potentials

$$\phi = \sum_k A_k \cosh(k(z+h)) e^{i(k \cdot \mathbf{w} - \omega_k t)} \quad (2)$$

$$\phi' = \sum_k (B_k e^{-kz} + C_k e^{kz}) e^{i(k \cdot \mathbf{w} - \omega_k t)} \quad (3)$$

for the bottom and top film, respectively. z and $\mathbf{w} = (x, y)$ are the coordinates in the vertical and horizontal directions, and we set $z = 0$ at the interface. The coefficients A_k , B_k , and C_k are related by the boundary conditions for pressure and vertical velocity component at the surface, the interface, and the substrate, in the form $B_k = [(\omega_0'^2 - \omega_k^2)/(\omega_0'^2 + \omega_k^2)] e^{2kh'} C_k$, and $A_k \sinh(kh) = C_k - B_k$.

For the limiting case of a binary-liquid system with infinite depths ($kh' \gg 1$; $kh \gg 1$), equation (1) reduces to the following limits:

(a) $\omega_+ \rightarrow \omega_0'$, which agrees, as it should, with the dispersion relation for a single liquid with density ρ' and surface tension α' . Therefore, the (+) mode characterizes a "surface mode" where only the top surface is excited.
(b) $\omega_- \rightarrow [\Delta\rho/(\rho + \rho')]^{1/2} \omega_0$; this mode characterizes an "interface mode" where the motion is essentially confined to the interface, and the top surface is almost at rest. We emphasize here that ω_- differs from $\omega_0 = (gk + \alpha k^3/\Delta\rho)^{1/2}$ which would describe a "pseudo-capillary surface mode" where $\Delta\rho$ replaces the liquid density, and α the surface tension.

3. Modified capillary wave model for a binary-liquid system

Capillary waves on the liquid surface and interface are excited by the thermal energy which has to provide:

(a) the kinetic energy

$$\varepsilon_k = (\rho/2) \int_{-h}^{\zeta} v^2 dz + (\rho'/2) \int_{\zeta}^{h+\zeta'} v'^2 dz,$$

(b) the surface and interface energy (for small slopes)

$$\varepsilon_s = (\alpha/2W) \int \nabla \zeta \cdot \nabla \zeta dx dy + (\alpha'/2W) \int \nabla \zeta' \cdot \nabla \zeta' dx dy,$$

where $W = \int dx dy$, and

(c) the gravitational energy

$$\varepsilon_g = \rho g \int_0^{\zeta} z dz + \rho' g \int_0^{\zeta'} z dz,$$

for the waves.

Here, ζ and ζ' are the interface and surface fluctuations. They can be expanded in the form $\zeta = \sum_k \zeta_k \exp(i(\mathbf{k} \cdot \mathbf{r} - \omega_k t))$ and $\zeta' = \sum_k \zeta'_k \exp(i(\mathbf{k} \cdot \mathbf{r} - \omega'_k t))$. The integrations for the energy terms can be carried out, using the boundary conditions, $v_z = \partial \phi / \partial z = \partial \zeta / \partial t$ at the interface, and $v'_z = \partial \phi' / \partial z = \partial \zeta' / \partial t$ at the surface. The total energy takes the simple harmonic oscillator form

$$\varepsilon = \frac{1}{2} \sum_k m_k \omega_k^2 \zeta_k^2 + \frac{1}{2} \sum_k m'_k \zeta'^2_k. \quad (4)$$

Here, we have introduced the effective mass $m_k = (4\pi^2/k) \times \{ (\Delta\rho \omega_0^2 / \omega_k^2) + \rho' \omega_k'^2 \omega_0'^2 / [\omega_k^2 \cosh(kh) - \omega_0'^2 \sinh(kh)]^2 \}$. According to the equipartition theorem the mean values of the two terms in equation (4) are equal.

The total fluctuating energy ε in equation (4) can also be expressed in terms of the surface fluctuations ζ' and ζ'' if m_k is replaced by $m'_k = [\cosh(kh) - \sinh(kh)(\omega_0'/\omega_k)^2] m_k$. Therefore, the mean square roughness $\langle \zeta'^2 \rangle$ can also be obtained using equation (5) (below) with m_k replaced by m'_k .

In thermal equilibrium, the mean energy of each oscillator is

$m_k \omega_k^2 \langle \zeta'^2_k \rangle = \hbar \omega_k / [\exp(\hbar \omega_k / k_B T) - 1]$, where k_B is the Boltzmann constant and T the temperature. Using the classical limit approximation, $\hbar \omega_k \ll k_B T$, we get from equation (4) the well-known result for the mean square interface amplitude:

$$\langle \zeta'^2 \rangle = \sum_k \langle \zeta'^2_k \rangle = \sum_k \frac{k_B T}{m_k \omega_k^2} \rightarrow k_B T \int_{k_{\min}}^{k_{\max}} \frac{2\pi k dk}{m_k \omega_k^2} \quad (5)$$

where the transition from the sum to the integral is well justified by the large number of modes. Equation (5) looks exactly like the usual expression for the interface roughness,^{1,4,5} if $m_k \omega_k^2$ is replaced by $4\pi^2(\Delta\rho/k)\omega_0^2$. Another difference is in the values for a high- k and a low- k cutoff, $k_{\max}$ and $k_{\min}$, described below. Furthermore, since for the composite liquid films there are two possible modes, $\omega_{\pm}$, there will be contributions to $\langle \zeta'^2 \rangle$ from both:

$\langle \zeta'^2 \rangle = \langle \zeta'^2_+ \rangle + \langle \zeta'^2_- \rangle$ where $\langle \zeta'^2_{\pm} \rangle$ is given by equation (5) with $m_{\pm}(k)\omega_{\pm}^2(k)$ inserted in the denominator.

The *high-k cutoff* is usually related to the molecular size d , setting $k_{\max} \approx d^{-1}$. We propose a more stringent limit: that determined by the validity of the potential flow assumption made here and in the standard capillary wave theory (which neglects the quadratic term ($\propto (\mathbf{v} \cdot \nabla) \mathbf{v}$) in the Navier-Stokes equation). This is justified only for $k \lesssim \langle \zeta'^2 \rangle^{-1/2}$ as shown in ref. 6. While effects of viscosity

vanish for potential flow (for which $\eta \nabla^2 \mathbf{v} = 0$, where η is the viscosity), viscosity attenuates the non-linear modes. Therefore, we use an effective upper cutoff $k_{\max} = \langle \zeta'^2 \rangle^{-1/2}$.

Even more stringent is a *lower cutoff* $k_{\min}$. For binary liquid systems, the potential flow given by (2) and (3) cannot satisfy continuity of horizontal velocity at the interface, $\phi(0) \neq \phi'(0)$. This gives rise to a slip $s = \sum_k (\mathbf{v}_{k \rightarrow} - \mathbf{v}'_{k \rightarrow}) / \omega_k$ at the interface, where $\mathbf{v}_{k \rightarrow}$ and $\mathbf{v}'_{k \rightarrow}$ are the horizontal velocities for the bottom and top liquids, respectively. To account for this "slip phenomenon", a low- k cutoff $k_{\min}$ is introduced to confine the slip to a plausible value. In the experiment studied here (Section 4) the two liquids are separated by a surfactant monolayer of thickness $\approx 30 \text{ \AA}$. Since the linear surfactant molecules used ($C_{10}E_4$) easily tilt away from their vertical orientation, this layer resembles a very soft, jelly-like medium, which can readily accommodate a horizontal slip as long as it does not exceed $\approx 10 \text{ \AA}$. A larger slip would require non-potential flow and therefore imply viscous damping. Thus, we take $10 \text{ \AA}$ as the practical upper limit of slip. This limit has a severe effect on calculated interface roughness, as shown in the following two examples.

(1) For the limiting case of a binary-liquid system with *infinite liquid depths* ($kh', kh \gg 1$), equation (5) gives:

(a) The interface roughness, as $\langle \zeta'^2_- \rangle = 0$,

$$\begin{aligned} \langle \zeta'^2 \rangle &= \langle \zeta'^2_+ \rangle \\ &= (k_B T / 4\pi\alpha) \ln \left[\frac{1 + c^2 k_{\max}^2}{1 + c^2 k_{\min}^2} \right] \end{aligned} \quad (6)$$

with the capillary length $c = (\alpha/g\Delta\rho)^{1/2}$. This indicates that the interfacial roughness is solely due to the interface mode which causes a slip $s = 2\zeta$.

(b) The surface roughness, as $\langle \zeta'^2_- \rangle = 0$,

$$\begin{aligned} \langle \zeta'^2 \rangle &= \langle \zeta'^2_+ \rangle \\ &= (k_B T / 4\pi\alpha') \ln \left[\frac{1 + c'^2 k_{\max}^2}{1 + c'^2 k_{\min}^2} \right] \end{aligned} \quad (7)$$

where $c' = (\alpha'/g\rho')^{1/2}$. This result shows that the surface roughness is solely due to the surface mode which causes no slip in this case.

(2) For the limiting case of a binary-liquid system with a *thin top film* ($kh' \ll 1$):

(a) The $(-)$ mode causing a slip of order of $\langle \zeta^2 \rangle^{1/2} / (kh')$ is strongly suppressed.

(b) The $(+)$ mode gives equal contributions to the surface and interface roughness

$$\begin{aligned} \langle \zeta'^2 \rangle &= \langle \zeta^2 \rangle \\ &= (k_B T / 4\pi(\alpha + \alpha')) \ln \left[\frac{1 + c''^2 k_{\max}^2}{1 + c''^2 k_{\min}^2} \right] \quad (8) \end{aligned}$$

where $c'' = [(\alpha + \alpha') / g\rho]^{1/2}$. This is equivalent to the roughness for a single liquid of density ρ and surface tension $\alpha + \alpha'$, indicating that the surface and interface fluctuate collectively. The fluctuations are suppressed by the increased effective surface tension due to the presence of the top film.

4. Experiment and results

We chose n-octane (C_8H_{18}), the non-ionic surfactant $C_{10}E_4$ (tetraethylene glycol monodecyl ether, molar weight 334.5 g/mol and density 0.951 g/cm³), and D_2O to form a binary-liquid system with a low interfacial tension at the oil-water interface²⁾ and a strong contrast in the scattering length density profile for neutrons.

A D_2O (purity 99.9%) surfactant solution containing a $C_{10}E_4$ molar concentration of 2.5×10^{-3} (above the critical micelle concentration of 6.4×10^{-4} measured in ref. 7) was placed into a flat Teflon sample holder with a 0.7 mm deep indentation of an area 18.9×8.5 cm². This sample was then sealed in a sample box (described in ref. 8) at $30.0^\circ\text{C} \pm 0.1^\circ\text{C}$. The time-of-flight neutron reflection measurements were conducted on the thermal neutron reflectometer at the Rhode Island Nuclear Science Center.⁹⁾

Instead of spreading the oil directly onto the surfactant solution, which had been shown to result in non-uniform coverage,¹⁰⁾ we deposited the oil through condensation of octane vapor to form an oil-water-surfactant system. For this purpose, a heated glass bottle containing 2-cm³ n-octane was placed in the sample box together with the surfactant solution. When the octane bottle was heated for 1 hr, the sample temperature increased to $(32.0 \pm 0.1)^\circ\text{C}$. We observed a pronounced decrease of reflected neutron intensity, indicating the formation of an oil film on the surfactant solution. Reflectivity data was collected when the intensity became stable. The results are shown in Figure 1.

In Figure 1 the reflectivity data for the surfactant solution is shown by open circles. The reflectivity (the reflected intensity divided by the incident intensity) is not unity in the total reflection region since the beam is only partially intercepted by the sample. The data were well fitted ($\chi^2 = 0.8 \pm 0.2$ per degree of freedom) to the Fresnel curve for pure D_2O with a Debye-Waller-like factor $\exp(-Q_z^2 \sigma^2)$, where $\sigma = (5 \pm 3) \text{ \AA}$ is the root-mean-square roughness for the air-liquid surface. This fitted surface roughness value agrees well with $\langle \zeta'^2 \rangle^{1/2} = 4.6 \text{ \AA}$ which was calculated using

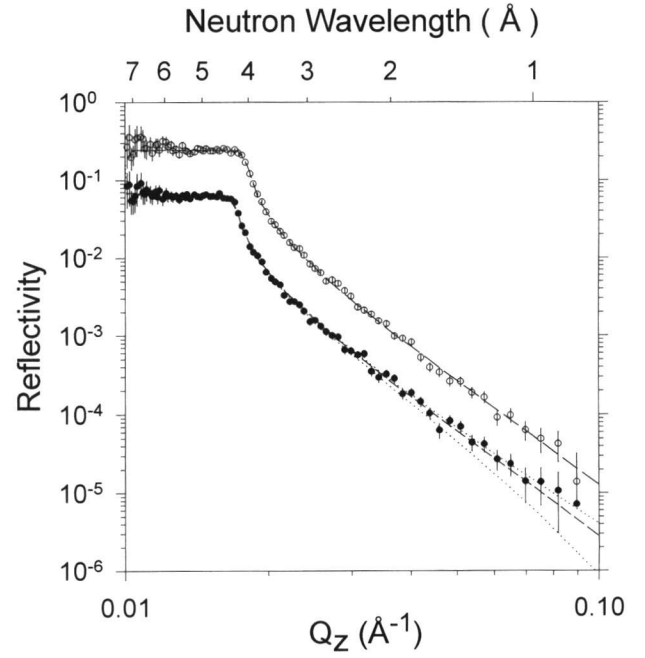


Figure 1: Reflection data versus momentum transfer Q_z for pure surfactant solution (open circles), fitted using the Fresnel reflectivity for D_2O and a surface roughness $\sigma = 5 \text{ \AA}$ (long dashed curve). The data for the oil-water-surfactant system (closed circles) were fitted using a two-layer model for the scattering length density profile representing a homogeneous oil layer floating on top of water (short dashed curve). The fitted oil-water interfacial roughness σ is $7 \text{ \AA}$. For comparison, the dotted curves above and below, calculated for $\sigma = 0 \text{ \AA}$ and $14 \text{ \AA}$, respectively, are clearly discernible.

Table I: Parameters for the two-layer model used to represent the data for the oil-water-surfactant system: ρb_c and Σ_i are the scattering length density and macroscopic incoherent scattering cross section density for each layer, respectively. $\sigma = \langle \zeta'^2 \rangle^{1/2}$ (or $\langle \zeta^2 \rangle^{1/2}$) is the root-mean-square roughness between the air and the top layer or between the top layer and the bottom layer. $\rho b_c = -0.52 \times 10^{-6} \text{ \AA}^{-2}$ for pure C_8H_{18} and $6.33 \times 10^{-6} \text{ \AA}^{-2}$ for 99.9% deuterated D_2O . $\Sigma_i = 5.34 \text{ cm}^{-1}$ for pure C_8H_{18} . The asterisk * designates quantities kept fixed in the fitting process. The reflectivity data is not sensitive enough to determine these quantities, due to the low contrast in the scattering length density between air and the oil film. The thickness of the top layer, however, is obtained using the incoherent scattering cross section density for octane.

	ρb_c ($10^{-6} \text{ \AA}^{-2}$)	Σ_i (cm^{-1})	Thickness (μm)	σ ($\text{\AA}$)
Top	-0.52*	5.34*	8.0 ± 0.3	0*
Bottom	5.73 ± 0.07	0.23	∞	7 ± 3

a surface tension of 30 dyn/cm as suggested in ref. 11, and a density of 1.1 g/cm³ for the surfactant solution.

The data (closed circles) measured for the oil-water-surfactant system show a reduced reflectivity due to loss suffered by the beam as it traverses the oil film. No significant reflectivity attenuation due to roughness was observed. A two-layer model for the scattering length density profile gives a good fit (dashed curve) to the data. The fitted parameters are summarized in Table I. They represent a top layer of oil floating on water containing 8%

oil. The oil layer thickness is $8.0\text{ }\mu\text{m}$ and the roughness σ of the oil-water interface is determined to be $(7 \pm 3)\text{ }\text{\AA}$.

Using the potentials and thickness given in Table I, the values $\alpha' = 22\text{ dyn/cm}$, $\alpha = 0.08\text{ dyn/cm}^2$, as well as cutoffs $k_{\text{max}} \approx 0.1\text{ }\text{\AA}^{-1}$, $k_{\text{min}} = 0$ for the (+) mode, and k_{min} almost equal to k_{max} for the (−) mode (thus restricting the slip to $\approx 10\text{ }\text{\AA}$), we obtain $\langle \zeta^2 \rangle^{1/2} \approx 6\text{ }\text{\AA}$ which is consistent with the measurement $(7 \pm 3)\text{ }\text{\AA}$. For comparison, application of the single-liquid capillary wave theory to the liquid-liquid interface as in ref. (1,4,5) yields a much larger value of $106\text{ }\text{\AA}$.

5. Conclusion

We have developed a modified capillary wave model for the surface and interface roughness of a binary-liquid system. The main features of this analysis on the basis of potential flow are the restrictions, k_{max} and k_{min} , imposed on the capillary wave spectrum. When the interfacial tension is low (less than a few dyn/cm) or the top film is thin ($kh' \ll 1$), the narrowing of the k region due to k_{min} is so significant that the (−) mode, which is responsible for a large slip at the interface, is strongly suppressed. This leads to the conclusion that the interfacial roughness between the real liquids may be smaller than often assumed. This conclusion is consistent with our interfacial roughness measurement for an octane- D_2O -surfactant binary-liquid system. Although the single-liquid capillary wave theory describes the surface roughness adequately, it cannot be adapted to the interfacial behavior between two liquids, especially when the interfacial tension is low, without taking into account the slip effect at the liquid-liquid interface.

However, several previous studies have reported interface roughness as large as about $100\text{ }\text{\AA}$.^{1,4,5} While these large values cannot be explained on the basis of potential flow alone, it is possible that the non-linear, attenuated waves, which we have neglected here, in fact contribute significantly to interface roughness. This problem should be studied in detail by solving the full Navier-Stokes equation including the non-linear and viscosity terms $(\alpha \nabla \cdot \nabla) \mathbf{v}$ and $\eta \nabla^2 \mathbf{v}$, respectively).

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