A molecular dynamics study of interfaces: from pure liquids to biological membranes

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Chapter 3

The interfacial broadening of a liquid-liquid interface*

3.1 Introduction

Most of the technological and biological processes occur at an interface. However the interface between two liquids is difficult to investigate [35,36] compared to two-phase systems as liquid-solid, solid-gas, or liquid-vapour, which exhibit large discrepancies in their molecular organization and densities, allowing extensive studies by a large range of experimental methods. Interfaces between oil and water are most widely studied since these interfaces are involved in major technological processes as crude oil extraction and detergent activity [37], and serve as models of biological hydrophilic-hydrophobic interfaces such as cell membranes [38,39].

Since many years, the analysis of the fluid interfacial organization has been both a theoretical and experimental challenge [40–49]. Recently, developments in experimental techniques (as x-ray reflectivity, diffuse surface x-ray scattering, grazing incidence x-ray diffraction and scattering, and the optical techniques) [50–54] combined with advances in molecular simulations because of improvements of computer performance, algorithms, and force fields, have dramatically extended the insight in properties of both liquid-vapour and liquid-liquid interfaces down to the molecular scale. However, bridging the gap between theoretical predictions from capillary wave and van der Waals theories [34], and simulation and experimental results, remains an exciting

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challenge.

The scope of this chapter is to study the molecular organization and properties of the liquid-liquid n-hexane–water interface and to compare them with the prediction from capillary wave theory. This leads us to a new definition of the correlation length, commonly used as a parameter in the roughness calculation. For an ordered interface, the amplitude of the capillary waves is reduced, possibly by the intermolecular interactions involving both the two liquid bulks and the interface.

3.2 Method and theory

3.2.1 Molecular dynamics

An all-atom model was employed to describe molecules at an atomic scale using the potential energy parameter set PARM27 from the CHARMM package [55]. The interactions include non-bonded dispersive and coulombic interactions, torsion, bond bending, and vibrational potentials. The TIP3P water model [56] was used and covalent bonds involving hydrogen were held fixed with the SHAKE algorithm [18]. Electrostatic interactions were computed using the Smooth Particle Mesh Ewald method [57]. We have prepared the simulation models as follows. Beforehand, a single box containing hexane molecules at the appropriate liquid density has been equilibrated. After this, we have built our complete simulation box by the addition of two boxes of vacuum on each side along the $z$ axis. We have relaxed the resulting box containing two liquid-vacuum interfaces parallel to the $xy$ plane. Finally, we have filled the empty volume by water molecules to reach the appropriate liquid density. In such a way, the system contains 448 hexane molecules, and about 3000 molecules of water, thus approximatively 18 000 atoms in a box of dimensions $L \times L \times L_z$ in the $x$, $y$, and $z$ directions respectively, with $L = 45 \, \text{Å}$, $L_z \approx 95 \, \text{Å}$, and the volume of each bulk phase is approximately equivalent. Consequently, the simulation boxes are large enough in the $z$ direction to avoid interactions between interfaces, and thus a dependence on $L_z$ of the interfacial width [58].

Molecular dynamics computer simulations were carried out using the DLPOLY package [59]. Our calculations were performed in the NVT ensemble [60], i.e., with constant temperature, volume, and number of particles. The equations of motion were solved using the Verlet Leapfrog integration algorithm [2] and simulations were run with periodic boundary conditions. For the van der Waals terms, calculations were performed using a cutoff radius of 12 Å. The liquid-liquid systems have been equilibrated during 100 000 steps,
3.2 Method and theory

with a time step of 2 fs, at four different temperatures: 283, 303, 323, and 343 K. During equilibration, the density profile and energy convergence of the system have been monitored. For the present study, we have run a simulation during 2 ns and recorded the dynamics of the system by accumulating coordinates at intervals of 0.4 ps during two periods of 0.4 ns.

3.2.2 Interfacial ordering and width

The water molecule by definition is a planar molecule. Its orientation is fully described by two orthogonal unit vectors: \( \vec{d}p \), parallel to the dipole moment, and \( \vec{n} \), perpendicular to the molecular plane. The \( n \)-hexane orientation is represented in this study by the longest principal axis of the molecule's ellipsoid of inertia, \( \vec{e} \). We have computed the molecular order parameter:

\[
S(z) = \frac{1}{2} \langle 3 \cos^2 \theta(z) - 1 \rangle ,
\]

where \( \theta \) is the angle between the vector \( \vec{d}p \), \( \vec{n} \) or \( \vec{e} \) and the interface normal vector.

Thermal fluctuations broaden a bare (sharp) interface to a width \( \sigma_{CW} \) as described by capillary wave theory [34,40]. This fluctuating bare interface is broadened (dressed) by an intrinsic width \( \sigma_0 \) [34,36,61]. Thus the interfacial roughness, or equivalently the total interfacial width \( \sigma \), is a combination of those two components:

\[
\sigma^2 = \sigma_0^2 + \sigma_{CW}^2 ,
\]

\[
\sigma_{CW}^2 \equiv \frac{k_B T}{4\pi^2\gamma} \int_{q_{\text{min}}}^{q_{\text{max}}} \frac{1}{q^2 + 2a^{-2}} \text{d}^2q ,
\]

where \( q \) represents the in-plane capillary waves, \( \gamma \) is the interfacial tension, \( a = 2\gamma/mg\Delta \rho \), \( \Delta \rho \) is the mass density difference between the two phases, and \( g \) is the gravitational acceleration.

The existence of capillary waves and their theoretical justification in both liquid-liquid and liquid-vapour systems is commonly accepted [35,36,54]. In computer simulations, from \( q_{\text{min}} \) which corresponds to \( 2\pi/L \) and \( q_{\text{max}} \) defined as \( 2\pi/\xi \) (where \( \xi \) is a correlation length), the capillary roughness expression 3.3 becomes [34,35]:

\[
\sigma_{CW}^2 = \frac{k_B T}{4\pi\gamma} \ln \frac{1 + 2(\pi a/\xi)^2}{1 + 2(\pi a/L)^2} .
\]
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Equation 3.4 shows that in the thermodynamic limit (the area $A = L^2 \to \infty$), the interfacial width diverges as $(-\ln g)^{1/2}$ if $g \to 0$. For a microscopic system such as the one considered in computer simulations, $\xi^2 \ll a \gg L^2$, so the expression 3.4 becomes:

$$\sigma_{CW}^2 = \frac{k_B T}{4\pi\gamma} \frac{L^2}{\ln \frac{1}{\xi^2}}$$

(3.5)

Despite the correlation length is defined as the shortest distance between two particles such as their motions are not correlated, it is often taken as either a molecular diameter or length. Since a liquid-liquid interface is formed of two correlated surfaces in close “contact”, the relevant correlation length is expected to be an average of those characteristic of the two molecular species (water and hexane in our case). Computer simulation studies of the dependence of $\sigma_{CW}$ on $L$ agree apparently with the logarithmic behaviour in formula 3.5 (see for example [62]).

In the recent literature on simulations and experiments [36, 63, 64], the intrinsic width $\sigma_0$ is less well established. This comes in part from the difficulty of independently evaluating $\sigma_0$ and $\sigma_{CW}$ [61]. In experiments far from criticality, for most liquid-vapour interfaces $\sigma_0^{liq-vap} \approx 0$ because $\sigma_{CW}$ alone accounts for $\sigma$. Consistently with $\sigma_0^{liq-vap} \approx 0$, the liquid-vapour density profiles $\rho(z)$ derived from atomic positions are best fitted with a form $\psi$ based on the error function $^{\dagger}$:

$$\psi(z) = \frac{1}{2} \left( (\rho^{liq} + \rho^{vap}) - (\rho^{liq} - \rho^{vap}) \operatorname{erf} \left[ \frac{(z - z_0)}{\sigma \sqrt{2}} \right] \right),$$

(3.6)

with:

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-t^2} dt$$

(3.7)

where $\rho^{liq}$ and $\rho^{vap}$ are the respective bulk densities of the liquid and vapour phases, $z_0$ the position of the Gibbs’ dividing surface, and $\sigma$ the interfacial width [62]. The width $\sigma$ obtained from the fit is directly proportional to the “90-10” width, defined as the width of the interfacial domain where $0.1\rho_{bulk} < \rho(z) < 0.9\rho_{bulk}$, by the relation $w_{90-10} = 1.82\sqrt{2}\sigma$.

$^{\dagger}$In [62], the authors explicitly set $\sigma^2 = \sigma_{CW}^2 + \sigma_0^2$, but do not provide any estimation of the intrinsic width.

$^{\dagger}$Sides et al. compare the relative merits of erf and tanh for $\psi$, and conclude in favour of the former when thermal fluctuations are dominating [62].
Immiscible liquid-liquid interfaces seem to allow an alternative definition for $\sigma_0$ [64]. It is well known that for these the two Gibbs' dividing surfaces do not coincide, such that a depletion is present at the interface. This is unambiguously revealed as a dip in the normalized total density profile $\varphi(z) = (\rho^A(z)/\rho^A) + (\rho^B(z)/\rho^B)$, where $\rho^A$ and $\rho^B$ are the bulk liquid densities of the two species $A$ and $B$. One approach consists in defining the intrinsic width as the distance between the Gibbs' surfaces of each component, $\sigma_0^{liq-liq} = |z_0^A - z_0^B|$ [64]. This corresponds to the assumption of the direct relation between the depletion and the intrinsic width $\sigma_0^{liq-liq}$. Keeping in mind $\sigma_0^{liq-vap} \approx 0$, the interpretation of the definition is as follows: place two immiscible fluid phases “in contact”, the equilibrium distance between their two bare surfaces is then determined by van der Waals, electrostatic, and intermolecular attractive and repulsive interactions. Furthermore, the minimum of $\varphi$ is for $z = z^{interface}$, the Gibbs’ dividing interface.

Obviously, the total density profile can be written as the sum of $\rho^A(z) + \rho^B(z)$ and be described accurately by:

$$\psi_{total}(z) = \frac{1}{2} \left( (\rho^A + \rho^B) - (\rho^A - \rho^B) \operatorname{erf} \left( \frac{(z - z_0)}{\sigma_{total} \sqrt{2}} \right) \right), \quad (3.8)$$

This is true as long as $\sigma_0^{liq-liq}$ is small compared to the interfacial widths for $\rho^A(z)$ and $\rho^B(z)$, and $\rho^A \neq \rho^B$.

Also, a composition profile can be used to characterize the interface:

$$\phi(z) = \frac{(\rho^A(z)/\rho^A) - (\rho^B(z)/\rho^B)}{(\rho^A(z)/\rho^A) + (\rho^B(z)/\rho^B)}, \quad (3.9)$$

By construction its midpoint coincides with $z^{interface}$. Irrespective of the depletion width and relative liquid densities, it is again well fitted by a relation similar to 3.6 or 3.8, with a width parameter $\sigma_{comp}$. 
3.3 Results

3.3.1 Molecular ordering

Figure 3.1 shows the density profile derived from atomic positions at 303 K, with two sharp water–hexane interfaces. At this temperature, the simulated bulk densities are in good agreement with the corresponding experimental densities. As the temperature increases, the hexane liquid density is overestimated, by approximately 4.5% at 343 K, its boiling temperature. Inversely, the water density is underestimated to a similar extent at high temperatures. Such small discrepancies suggest that the set of parameters used in our simulations may not be optimal for high temperatures.

Figure 3.2 shows the normalized total density profiles $\varphi(z)$ close to the interface, which position is taken from the fit of the composition profile $\phi(z)$. The oil phase presents a slight layering, compared to the water phase which flattens immediately beyond the interface region. Those normalized density profiles evidence clearly a depletion at the interface, characteristic of an interface between two immiscible fluids.

Figures 3.3 and 3.4 give the molecular order parameters of hexane and water as a function of their distance from the interface. From the relation 3.1, we see that the order parameter is equal to $-0.5$ when the considered vector is parallel to the interface, is equal to $1$ when the vector is normal to the interface, and $0$ represents a random distribution (or a distribution centred on 54 degrees). From these two graphs, we see that both phases possess a degree of ordering extending from about 7 Å in the bulk phase to about 4 Å in the other phase.

At the interface, hexane molecules have a preferential orientation parallel to the interface (from about 65 degrees at 283 K to 60 degrees at 343 K, relative to the interface normal). There, the water dipoles adopt the same orientation as hexane molecules, but this orientation is conserved by the water molecules far into the oil side. The normal vector orientation has a different behaviour with a maximum value at the interface (corresponding to a preferential angle of about 50 degrees) and an increasing disorder as the molecules are located deeper in the oil region. This global orientation of water molecules at the interface with the oil phase is in agreement with results reviewed by Pratt and Pohorille [38].

At a distance of 4 – 7 Å from the interface, the hexane curves display a slightly positive value of the order parameter, unlike the water curves. This difference in the profiles might be related to the stiffness and the length of the hexane molecule compared to the water molecule.
3.3 Results

Figure 3.1: Atomic density profiles at 303 K for water $\rho^w(z)$ (dotted), hexane $\rho^h(z)$ (dashed), and water+hexane $\rho^h(z) + \rho^w(z)$ (solid line).

Figure 3.2: Normalized density profiles $\varphi(z)$ at one interface as a function of the distance from the interface (see the text for the calculation of the interface position), at 283, 303, 323, and 343 K. The oil phase corresponds to the positive values of $z$, and the water phase to the negative values.
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Figure 3.3: Order parameters for hexane molecules as a function of their distance from the interface at 283, 303, 323, and 343 K. The hexane phase corresponds to positive values of the distance. Data are averaged over the two interfaces. On the left side, the curves are noisier due to a smaller statistical accuracy.

Figure 3.4: Order parameters for water molecules as a function of their distance from the interface at 283, 303, 323, and 343 K. The water phase corresponds to negative values of the distance. Both contributions from the dipole and normal vectors are reported. Data are averaged over the two interfaces. On the right side, the curves are noisier due to a smaller statistical accuracy.
3.3 Results

To complete the description of the interfacial organization, we have computed the orientation of the projection of the hexane molecular director in the interfacial plane. No preferential orientation is noticeable, implying that hexane molecules are disordered in the plane of the interface (data not shown).

For both the hexane and the water molecules, increased temperature reduces the ordering at the interface. This can be related to an alteration of the hydrogen bond network for the aqueous phase and an enhancement of the dynamics of molecules, as the temperature increases.

3.3.2 Interfacial tension

Figure 3.5 reports the pressure profiles $P_N - P_T$ as a function of the temperature. The pressure profile is zero in the two bulk phases. At the interface, the charged water molecules are ordered. This peculiar organization yields a polarization of the interfacial molecular layer, corresponding to a negative pressure profile. Inversely, the oil phase, with a low electron density and a reduced ordering (molecules are only ordered parallel to the interface, with no in-plane order), has no electrostatic contribution to the pressure profile.

As the ordering of molecules at the interface, the interfacial tension (from relation 2.6) decreases with the temperature. Computed values of interfacial tension are compared with experimental results $\gamma_{exp}$ [53] in Table 3.1. Our results are about $9-10\%$ smaller than experimental results, except for the
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<table>
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<th>T (K)</th>
<th>( \sigma^w )</th>
<th>( \sigma^h )</th>
<th>( \sigma^h-w_\text{total} )</th>
<th>( \sigma^h-w_\text{comp} )</th>
<th>( \gamma_{\text{sim}} )</th>
<th>( \gamma_{\text{exp}} ) ( (mN.m^{-1}) )</th>
<th>( \xi' )</th>
<th>( \xi'' )</th>
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<td>0.64</td>
<td>2.10</td>
<td>41</td>
<td>46.4*</td>
</tr>
</tbody>
</table>

Table 3.1: Fitted surface widths (\( \sigma^w \) and \( \sigma^h \)), interfacial widths (\( \sigma^{h-w} \), \( \sigma^{h-w}_{\text{total}} \), \( \sigma^{h-w}_{\text{comp}} \)), intrinsic width (\( \sigma^{h-w}_0 \)), computed capillary wave width (\( \sigma_{\text{CW}}^{h-w} \)), experimental (\( \gamma_{\text{exp}} \)) [53] and computed (\( \gamma_{\text{sim}} \)) interfacial tensions, and corrected correlation lengths (\( \xi' \) and \( \xi'' \)). The computed interfacial tensions are defined with an error bar of \( \pm 1.6mN.m^{-1} \). (* extrapolated value from Zeppieri results [53])

lowest temperature where the computed interfacial tension is greater than the experimental interfacial tension. For this latter case, the representation of the system at the lower temperature may not reproduce the experimental liquid-liquid interface with an expected accuracy. The estimation of the interfacial tension for a liquid-liquid system is improved compared to the calculation of the surface tension of a liquid-vapour system done with the same method [65]. This is likely due to the consideration of the electrostatic term in the force field. It is worth noticing that our calculation, which is performed without any long range correction, yields an underestimation independent of the system studied [65,66], while calculations with a long range correction yield an underestimation of the interfacial tension for short alkanes and an overestimation for the longer ones [63].

### 3.3.3 Interfacial width

The correlation length \( \xi \) is a parameter for the interfacial width resulting from thermal fluctuations. As reported above, while its definition is well established, its choice is not discussed in the literature and, as mentioned, \( \xi \) is always estimated as/from either the diameter or the length of one of the two molecules. Since \( \xi \) is located in the logarithm of the relation 3.5, one might consider that its order of magnitude is sufficient to estimate correctly the interfacial width \( \sigma_{\text{CW}} \).

Still, Akino and coworkers [67] pointed out that for a nematic phase of ellipsoid molecules placed at an interface, the amplitude of capillary waves in a direction parallel to the ellipse director is smaller compared to the amplitude of the waves perpendicular to the molecular axis. Consequently, we assume
that the larger wave amplitude, responsible for the interfacial widening, is related to the molecular diameter and not the molecular length. We have chosen $\xi$ as equal to the hexane molecular diameter, thus approximately 4 Å. This value is close to the value of the water molecular diameter, 3.2 Å. The capillary widths obtained from this choice of $\xi$, and using our computed values of interfacial tension, are reported in Table 3.1.

We have fitted to an error function (see formulas 3.6 and 3.8) the density profiles related to the hexane, the water, the total, and the composition density profiles (as defined by equation 3.9). In these formulas, we fixed the bulk density parameters and fitted the interface parameters: $z_0$ and $\sigma$. Figure 3.6 shows the difference between the fitting curves and the corresponding density profiles. This difference allows both a qualitative and quantitative estimation of the goodness of the fits. In the region delimited from $-5$ Å to $+10$ Å the plots present some small features which are not centred on the Gibbs’ dividing surface but mainly occur at the hexane surface. They originate from the features observed on the hexane density profile at the interface (Figure 3.1). Outside this region, the difference corresponds to microscopic fluctuations of the density profile. The fitted $\sigma$ parameters are reported in Table 3.1. Strikingly, $\sigma_{CW}$ is consistently larger than $\sigma_{total}$ by 50% and $\sigma_{comp}$ by 25%. This trend is also present in other works, see for example [68]. This situation precludes validating directly the capillary wave theory model of the interface, and a fortiori the hybrid model (relation 3.2).

The intrinsic width $\sigma^{liq-liq}_{0}$ corresponds to about one third of $\sigma_{total}$ (see Table 3.1). Together with the small deviations observed on figure 3.6, this justifies using formula 3.8 to represent the total density profile. The normalized density profiles give “90-90” widths fully consistent with $\sigma^{liq-liq}_{0}$. It is worth noticing that the intrinsic width as computed in this article depends on the temperature and is not the width computed between the two inflection points of the normalized density profiles [69].

### 3.4 Discussion

To the best of our knowledge, there has been no published account of simulation studies aiming at verifying accurately the interrelations between $\sigma_0$, $\gamma$, and $\xi$ for liquid-liquid interfaces. Therefore the following discussion attempts to resolve the disagreement with capillary wave theory.

While questionable, the use of the experimental interfacial tension instead of the computed value cannot explain the amplitude of the observed discrepancy. Rather, we focus on the order at the interface, which has been
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Figure 3.6: Difference between \( \rho^h(z) \), \( \rho^w(z) \), \( \rho^h(z) + \rho^w(z) \), and \( \phi(z) \), density profiles, and their fitting function at a temperature of 303 K. The interfacial position has been determined from the fit of \( \phi(z) \).

found in other simulations of alkane-water interfaces [38,63,68,70,71]. From their X-ray scattering experiments, Schlossman and coworkers do not exclude such an interfacial organization [72,73]. While it involves both surfaces, one might expect a screening of certain capillary modes. In the case of a nematic interface [67], this screening is observable in the direction parallel to the molecular director. In the case of the hexane–water liquid-liquid system, since the hexane molecules are disordered in the plane at the interface, the screening occurs isotropically in-plane, yielding a dramatic reduction in the effect of the thermal fluctuations.

Consequently, one needs to specify better the parameter \( \xi \) for ordered interfaces. Two conventions coexist in the literature. Concerning thin films located at the interface (in fact similar to the interfacial layer of a pure liquid) the correlation length refers to the transverse correlation length [58], while for an interface between two ideal liquid phases, this correlation length is taken as the bulk correlation length. In our case, molecular motions at the interface result from two kinds of interactions, those from the underlying bulk (more accurately from the two bulks in the case of an interface) and those between the molecules making up the interface. Thus, the correlation length must correspond to a combination of the two definitions given above. In order to estimate a corrected value of the correlation length, we have fitted to \( \sigma_{\text{total}} \) (resp. \( \sigma_{\text{comp}} \)) the prediction from relation 3.2 with only \( \xi \equiv \xi' \) (resp. \( \xi'' \)) as a
free parameter, using the computed value of $\sigma_{\text{liq-liq}}^{\text{liq-liq}}$ reported in the table 3.1. The resulting values for $\xi'$ and $\xi''$ are given in the same table. $\xi'$ shows a decrease from 19.7 Å (less than half of the simulation box) at 303 K, to 15.9 Å at 343 K, in keeping with the behaviour of $\sigma_{\text{total}}$. On the other hand, $\xi''$ is almost constant in this range of temperatures. Because the data at the lowest temperature might not represent accurately the experimental interface, it is difficult to conclude on the significance of the correlation lengths at 283 K relative to those of the higher temperatures.

It is interesting to use $\xi'$ and $\xi''$ for predicting measured capillary widths. For this purpose, we use $\gamma_{\text{exp}}$ [53] and $L_{\text{exp}}$ [74] in relation 3.5: the values of $\sigma_{\text{CW}}$ obtained together with the corrected correlation lengths are then smaller than the experimental widths for hexane–water measured by X-ray scattering in reference [74]. The difference corresponds likely to some intrinsic width $\sigma_{0}^{\text{liq-liq}}$. Ours is far too small to recover the observed width. Taking for $\sigma_{0}^{\text{liq-liq}}$ the radius of gyration of the alkane [72] seems to work better ($R_g = 2$ Å for hexane). The situation is summarized in figure 3.7, at the temperature 303 K close to experimental conditions of [74].

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**Figure 3.7:** Variation of $(\sigma_{\text{CW}}^{h-w})^2$ against the correlation length $\xi$, at 303 K. The bottom curve uses an upper cutoff $q_{\text{max}} = 2\pi/L$ to describe our simulations. The top curve uses a cutoff $q_{\text{max}} = 2\pi/L_{\text{exp}}$ to describe the experiments of Schlossman and coworkers [72]. Horizontal lines refer to the observed $\sigma_{\text{exp}}^{h-w}$ in simulation and $\sigma_{\text{total}}$ in experiment. Below $\xi = 10$ Å the capillary wave model cannot be consistent with the simulated $\sigma$. 

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- Discussio n
- 3.4 Discussion
- $\sigma_{\text{CW}}$(sim)
- $\sigma_{\text{comp}}$(sim)
- $\sigma$(exp)
- $\sigma_{\text{CW}}$(exp)
Concluding remarks

A careful study of the ordered interface between two immiscible fluids reveals the disagreement between the actual interfacial width and its prediction from the capillary wave theory. The discrepancy can be resolved by using a correlation length consistent with the molecular organization at the interface. So improved, our prediction is compatible with experimental results. Further studies require to fully characterize the intrinsic width, so as to provide a firmer basis to our hypothesis.