Computer Simulation Study of the Interface Width of the Liquid/Liquid Interface

Sanjib Senapati and Max L. Berkowitz

Department of Chemistry CB 3290, University of North Carolina, Chapel Hill, North Carolina 27599
(Received 30 May 2001; published 4 October 2001)

Four molecular dynamics computer simulations have been performed to study the intrinsic width and the width due to thermal fluctuations of the water/carbon tetrachloride interface. We observed that thermal fluctuations have a capillary wave character. The surface tension calculated by using capillary wave formalism shows a very good agreement with the value obtained from the components of the pressure tensor.

Detailed knowledge of the structure and dynamics of the liquid/liquid interface is needed to solve many problems of considerable technological importance. Because of its nature as a buried interface, very few experimental techniques can directly probe the molecular detailed picture of such an interface. The experimental data are often interpreted using an assumption that total interfacial width contains two components: an intrinsic component and a component due to capillary waves. For example, in the case of light reflection experiments, it was shown [1,2] that data on ellipticity coefficients were best fitted when both components were taken into account. Very recently, x-ray reflectivity studies [3,4] and neutron reflectivity studies [5] provided us with accurate measurements of the interfacial width of the water/organic interface. The x-ray reflectivity studies even allowed us to resolve a long-standing question of how much of the interface width is due to the intrinsic width and how much is due to the broadening caused by capillary waves [4].

A number of computer simulations were performed to study liquid/liquid interfaces (for a review, see Ref. [6]). The density profiles obtained from these simulations were consistent with the ones predicted by capillary wave theory and, in one case (water/lipid membrane interface), it was shown that the fluctuation spectrum of the interface has a signature predicted by this theory [7]. We are not aware of any simulation where a separation of the interface width into an intrinsic component and a component due to capillary wave broadening was performed. In what follows, we will describe our attempt to do this using the results we obtained from water/carbon tetrachloride computer simulations.

For the present study, we performed a series of four molecular dynamics simulations on a carbon tetrachloride/water/carbon tetrachloride system. Each member of the series differed by its surface area. We have used the SPC/E [8] model of rigid water (the rigidity of water was kept by using the SHAKE algorithm [9]). For carbon tetrachloride, we used a fully flexible, nonpolarizable, five-site model [10]. The potential parameters used in these simulations can be found in Table 3 of Ref. [10]. Periodic

boundary conditions were applied in three dimensions for all the simulations.

Simulations of liquid/liquid interfaces can be performed using different ensembles [11]. We performed our simulations using the NP_nAH ensemble that belongs to a class of the "extended" ensembles first introduced by Andersen to perform molecular dynamics simulations under constant pressure [12]. The appropriate equations of motion for particles simulated in this ensemble are given in Ref. [11].

Our carbon tetrachloride/water/carbon tetrachloride systems were constructed by combining three boxes which contained pure carbon tetrachloride, pure water, and pure carbon tetrachloride molecules, respectively. All of these boxes had the same cross section area, and their dimensions along the x and y directions were chosen to be equal. The three liquids were equilibrated initially for 300 ps. Then the boxes were combined into one single box. The cross section and L_z (the box length along the z direction) of the final simulation boxes were chosen so that the correct bulk density of water (0.997 g/cm^3) and of carbon tetrachloride (1.59 g/cm^3) were achieved in the bulk regions. For every system, we used the following equilibration procedure: (i) We performed energy minimization for 1000 steps. (ii) Following the minimization, we performed 300 ps of molecular dynamics in the canonical (NVT) ensemble with initial velocities selected from a Maxwellian distribution at 300 K. The system was coupled to an external heat bath at 300 K with a coupling time constant $\tau = 0.5$ ps. (iii) Finally, we performed a 100 ps molecular dynamics run at constant NP_nAH, with P_n equal to 1 atm. This last simulation at constant NP_nAH provided the initial conditions for the production run of 400 ps in each system. The temperature of the run was 300 K.

The production runs consisted of eight blocks of 25 000 steps performed in the NP_nAH ensemble. In each block, the density profile, the normal and tangential components of the pressure tensor, and the surface tension were calculated every 20 steps. The fluctuations in the densities and surface tension were estimated using the variation in the block averages. The number of particles and the dimensions of the box in each simulation are

shown in Table I. All simulations were carried out using DLPOLY molecular dynamics simulation package [13] appropriately modified for use of the NP_nAH ensemble. Long range forces were taken into account following an Ewald scheme. The real space part of the Ewald sum and Lennard-Jones interactions were cut off at 9 Å. The mass of the pressure piston was set to 500 amu in all the systems, and the time step was 0.002 ps.

From the thermodynamics point of view, the interface is characterized by such quantities as surface tension and interface width. Unlike a somewhat fuzzy concept of the interfacial width, the surface tension of liquid/liquid system is well defined. When the interface is perpendicular to the z axis, the surface tension (γ) is given by the following equation [14]:

$$\gamma = \int_{-\infty}^{+\infty} dz \, [P_n - P_t(z)], \tag{1}$$

where P_n and P_t are normal and tangential pressures, respectively. For a planar interface, P_n is uniform, however, P_t strongly depends on the position z. At a point far from the interface, $P_t = P_n = P$. Therefore, only the region near the interface contributes to the integral. If we define the averaged tangential pressure over the simulation box as

$$P_t = \frac{1}{2L_z} \int_{-(1/2)L_z}^{+(1/2)L_z} dz \, [P_{xx}(z) + P_{yy}(z)], \tag{2}$$

then the equation for the surface tension can be rewritten as

$$\gamma = L_z(P_n - P_t). \tag{3}$$

Considering that we have two interfaces and that the height of the box L_z is varying,

$$\gamma = \tfrac{1}{2}\langle L_z(P_n - P_t)\rangle, \tag{4}$$

where the angular brackets denote the average over trajectory. We used Eq. (4) to obtain the value of the surface tension from the pressure calculations. The surface tension can be also obtained through the calculation of the width of the interface. If one treats thermal fluctuations according to capillary wave theory, one gets the following relationship between the width w_c due to capillary broadening and the surface tension [14]:

$$w_c^2 = \frac{k_B T}{2\pi\gamma} \ln\!\left(\frac{L_\parallel}{l_b}\right), \tag{5}$$

where k_B is the Boltzmann constant, $L_\parallel$ is the size along the x or y dimension of the box, and l_b is the bulk correlation length, which is of the order of molecular length.

The dimensions of the unit cell for all four simulations are listed in Table I. As expected, for simulations in the NP_nAH ensemble, the box length along the z direction L_z, fluctuates over the course of the simulation. We observed that the average value of L_z grew slightly during the course of 100 ps equilibration at constant NP_nAH, indicating a slight initial expansion of the box along the z direction. This is expected, because of the repulsion between the water and the carbon tetrachloride molecules. During the production run, the box length L_z fluctuated around the average given in Table I. The average normal pressure for all the four simulations fluctuated around the reference value of 1 atm. In a few cases, the fluctuations were quite extensive (± 25 atm), but we did not observe any noticeable drift. The tangential pressure, as expected, showed a high negative value, thus producing a nonzero surface tension in our system. The surface tension at the carbon tetrachloride/water interface was calculated from the diagonal elements of the molecular pressure tensor using Eq. (4). These values obtained from each simulation are also shown in Table I, and the average surface tension obtained from the four simulations is 53.05 ± 6.5 mN/m. The experimental value at 293 K is 45.0 mN/m [15].

To study the width of the interface, we calculated the density profile as a function of the z coordinate. In Fig. 1 we show the mass density profile for the system containing 432 carbon tetrachloride and 875 water molecules. These profiles are obtained by dividing the entire simulation cell into 0.2 Å slabs parallel to the xy plane, and then assigning molecules into the corresponding slab. The profiles show two stable and relatively smooth interfaces, thus indicating that the potential model we have chosen successfully describes formation of the interfaces. The average bulk densities are in good agreement with the experimental values. The average carbon tetrachloride density in the slab corresponding to $+25 \leq z \leq +40$ Å is 1.56 g/cm^3, which is very close to the experimental value of 1.59 g/cm^3. The average water density in the central slab corresponding to $-5 \leq z \leq 5$ Å is 0.988 g/cm^3. The experimental value is 0.997 g/cm^3. The density profiles from our simulations look similar to the density profiles obtained by Chang and Dang [16], although they used different sized system and polarizable potentials. Small fluctuations are present in our

TABLE I. Number of molecules, dimensions of the unit cells, width, and surface tensions in four simulations. w_0 is the intrinsic width, and w_c is the width due to capillary broadening of the interface. γ_p is the surface tension obtained through the calculation of the pressure tensor, and γ_c is the surface tension obtained through the calculation of the thermal width.

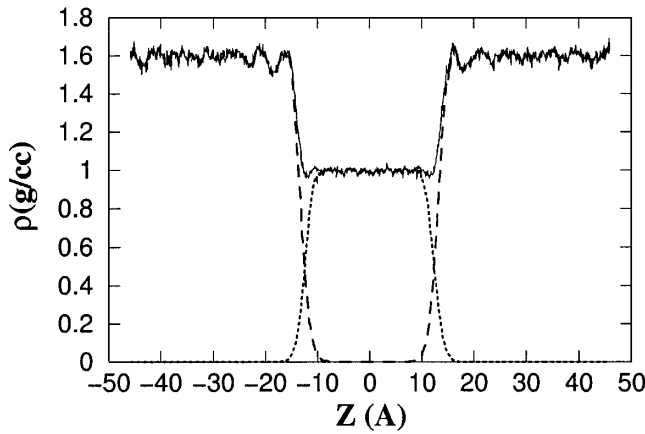| System	No. of H$_2$O	No. of CCl$_4$	$L_\parallel$ (Å)	L_z (Å)	w_0 (Å)	w_c (Å)	γ_P (mN/m)	γ_c (mN/m)
1	875	432	32.55	89.96	0.65	1.58	56.28 ± 6.9	54.33
2	1813	686	37.94	113.82	0.64	1.60	50.62 ± 5.7	56.92
3	2744	1024	43.40	130.20	0.75	1.68	56.27 ± 7.2	54.77
4	2465	1134	48.82	107.02	0.70	1.71	53.13 ± 6.3	55.52

FIG. 1. Densities of water (dotted line), carbon tetrachloride (dashed line), and total (solid line) for the simulation with 432 carbon tetrachloride and 875 water molecules.

density profiles which could be an artifact of the relatively short simulation time. Nevertheless, our density profiles for carbon tetrachloride are smoother than the ones from the simulations of Chang and Dang, perhaps because we simulate a larger sized sample.

The fluid density in the interfacial region is often given by the following equation:

$$\rho(z) = \frac{1}{2}(\rho_1 + \rho_2) - \frac{1}{2}(\rho_1 - \rho_2)\mathrm{erf}\left(\frac{1}{\sqrt{2}\,w_c}\right),$$

(6)

where erf is the error function, ρ_α is the bulk density of the αth component, and w_c is the width of the interface due to thermal fluctuations of this interface [6]. The last formula is obtained using the assumption that these fluctuations have a Gaussian character. To get the last formula, let us assume first that liquids 1 and 2 create a sharp interface. In this case, we can write the following for liquid 1:

$$\rho_1(z) = \rho_1\theta[h(s) - z],$$

(7)

where θ is the step function and $s = (x, y)$. Similarly, for liquid 2 we can write

$$\rho_2(z) = \rho_2\{1 - \theta[h(s) - z]\}.$$

(8)

Differentiate Eqs. (7) and (8) and get

$$d\rho_1(z)/dz = -\rho_1\delta[h(s) - z],$$

(9)

$$d\rho_2(z)/dz = \rho_2\delta[h(s) - z].$$

(10)

Now assume that the interface has a finite width and replace δ functions in the last two equations with Gaussian distributions of the same width, integrate the equations, and get

$$\rho_1(z) = \frac{1}{2}\rho_1 - \frac{1}{2}\rho_1\mathrm{erf}\left(\frac{z - \langle h_1\rangle}{\sqrt{2}\,w_c}\right),$$

(11)

$$\rho_2(z) = \frac{1}{2}\rho_2 + \frac{1}{2}\rho_2\mathrm{erf}\left(\frac{z - \langle h_2\rangle}{\sqrt{2}\,w_c}\right),$$

(12)

where $\langle h_1\rangle$ and $\langle h_2\rangle$ are average positions of the interface for liquids 1 and 2, respectively. If we assume that no

intrinsic interface is present $\langle h_1\rangle = \langle h_2\rangle = \langle h\rangle$. Adding Eqs. (11) and (12) and setting $\langle h\rangle = 0$ produces Eq. (6). If the internal width is present in the system, we can fit Eqs. (11) and (12) to the density curves for liquids 1 and 2 obtained from the simulation. The fit will give us the values of the intrinsic width $w_0 = |h_1 - h_2|$ and the width due to fluctuations—w_c.

We fitted our density profiles to the functions given by Eqs. (11) and (12) and obtained the values for the internal width and thermal width for every simulation. These values are also given in Table I. The table shows that the intrinsic width that should not depend on the surface area indeed does not display any regular trend in the simulations, while the width due to thermal fluctuations is increasing with the interface area in agreement with Eq. (5). To get the value of the surface tension using the fluctuation formula given by Eq. (5), we need to know the value of l_b. This can be estimated to be the average distance between water and carbon tetrachloride molecules $\sigma_{av} = 0.5\,(\sigma_{ct} + \sigma_w) = 4.3$ Å. We can also extract the value of the bulk length using our simulations. From Eq. (5), we get the following equation for the surface tension:

$$\gamma_{ij} = \frac{k_B T}{2\pi[(w_c^2)_i - (w_c^2)_j]}\ln(L_{\parallel,i}/L_{\parallel,j}),$$

(13)

where i and j stand for ith and jth simulation runs performed at corresponding $L_{\parallel,i}$ and $L_{\parallel,j}$; γ_{ij} is the surface tension obtained using the data from simulations i and j. The advantage of the last formula is that it allows one to get the value of the surface tension independent of the value of the parameter l_b. We calculated γ_{41}, γ_{42}, and γ_{31} (we used these combinations because they correspond to the largest differences in widths that appear in the denominator) using Eq. (13), averaged the values, and obtained surface tension equal to 55.44 mN/m.

If the value of the surface tension is known, we can invert Eq. (5) and get the following for the bulk correlation length:

$$l_b = L_{\parallel}\exp(-2\pi\gamma w_c^2/k_B T).$$

(14)

We used the value of 55.44 mN/m for surface tension and obtained l_b for every run with the average $l_b = 4.16$ Å, in excellent agreement with an estimate based on the size of the molecules.

Table I also shows the values of the surface tensions obtained from Eq. (5). The results are somewhat sensitive to the value of l_b, but a 20% change in l_b produces a change in the surface tension that is less than 10%. Finally, to check that thermal fluctuations are indeed of capillary wave character, we, following the work of Sides et al. [17] plotted w_c^2 vs $\ln\left(\frac{L_{\parallel}}{l_b}\right)$ as shown in Fig. 2. As we can see from the figure, the four points from the four simulations indeed lay on a straight line that goes through the origin of coordinates, thus confirming the capillary wave
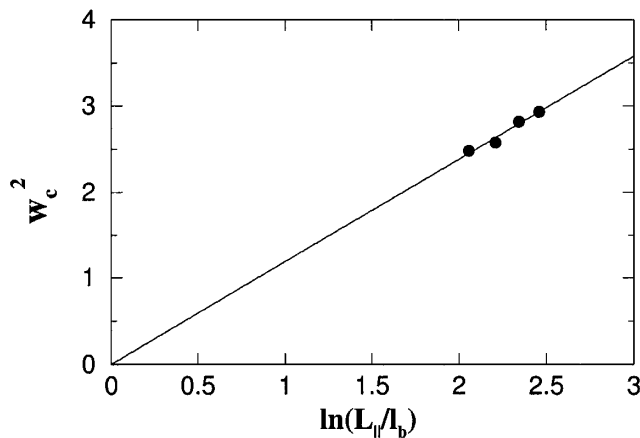
FIG. 2.   Square of the width due to thermal fluctuations as a function of the $\ln(L_{\parallel}/l_b)$.

character of the fluctuations. A linear least-square fit through the data results in a value of surface tension $\gamma = 55.3$ mN/m. Note that all the different values we obtained for surface tension using capillary wave theory are in excellent agreement with each other and are in good agreement with the value obtained via pressure tensor calculations.

An important quantity characterizing the interface is its width. It arises due to the intermixing of the two liquids, which may occur to a certain degree at zero temperature giving rise to an intrinsic width. In addition, capillary wave theory predicts that thermally excited fluctuations in the position of the interface give rise to an additional component of the width. This broadening primarily depends on the surface tension, the temperature, and the cross-sectional area of the interface. In our simulations of the water/carbon tetrachloride interface, we separated the interfacial width into two components and found that the intrinsic width is small, but finite ($w_0 \sim 0.7$ Å). The width due to thermal fluctuations is indeed having a capillary wave character and for our size of the interface has a value which is about twice the value of the intrinsic width. If we scale up the interface to the size for which the experimental observations using x-ray reflections were made, the value of the thermal width will at least double. In this case, we observe that our numbers for the width components and the numbers reported in Ref. [4] are consistent with each other.

We also calculated the surface tension of the interface in two different ways: (i) by using the pressure equation and (ii) through the equation obtained from the capillary wave theory. The two calculations produced results that are in very good agreement with each other. Finally, using our simulations we calculated the correlation length. The result we obtained from these calculations is in excellent agreement with the length obtained from the estimate based on molecular sizes.

[1] V. L. Kuzmin and V. P. Romanov, Phys. Rev. E **49**, 2949 (1994).
[2] A. Mukhopadhyay and B. M. Law, Phys. Rev. E **63**, 011507 (2000).
[3] D. M. Mitriniovic, Z. Zhang, S. Williams, Z. Huang, and M. L. Schlossman, J. Phys. Chem. B **103**, 1779 (1999).
[4] D. M. Mitrinovic, A. M. Tikhonov, M. Li, Z. Huang, and M. L. Schlossman, Phys. Rev. Lett. **85**, 582 (2000).
[5] J. Bowers, A. Zarbakhsh, J. R. P. Webster, L. Hutcandhings, and R. W. Richards, Langmuir **17**, 140 (2001).
[6] I. Benjamin, Annu. Rev. Phys. Chem. **48**, 407 (1997).
[7] M. A. Wilson and A. Pohorille, J. Am. Chem. Soc. **116**, 1490 (1994).
[8] H. J. C. Berendsen, J. R. Grigera, and T. P. Straatsma, J. Phys. Chem. **91**, 6269 (1987).
[9] G. Cicotti and J. P. Ryckaert, Comput. Phys. Rep. **4**, 345 (1986).
[10] K. J. Schweighofer, U. Essmann, and M. Berkowitz, J. Phys. Chem. B **101**, 3793 (1997).
[11] Y. Zhang, S. E. Feller, B. R. Brooks, and R. W. Pastor, J. Chem. Phys. **103**, 10 252 (1995).
[12] H. C. Andersen, J. Chem. Phys. **72**, 2384 (1980).
[13] W. Smith and T. R. Forester, DLPOLY (2.12 version); CCLRC, Daresbury Laboratory, 1999.
[14] J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Clarendon, Oxford, 1982).
[15] H. Ted Davis, *Statistical Mechanics of Phases, Interfaces, and Thin Films* (VCH, New York, 1996).
[16] T.-M. Chang and L. X. Dang, J. Chem. Phys. **104**, 6772 (1996).
[17] S. W. Sides, G. S. Grest, and M. Lacasse, Phys. Rev. E **60**, 6708 (1999).