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# Predicting Interfacial Tension between Water and Nonpolar Fluids from a Cahn-Type Theory

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We propose an accurate method to predict interfacial tension between water and nonpolar fluids by using Cahn gradient theory. The only necessary elements are (i) a water contact energy function and (ii) an equation of state (EoS) for the nonpolar fluid, chosen here as the Peng–Robinson EoS. The contact energy, a function of the fluid (adsorbate) surface density, is related to interfacial tension (IFT) by means of the Gibbs adsorption equation. Examining a large number of IFT data, we observe that the water contact energy is a universal function of adsorbate's surface density when proper scaling variables are used: it depends neither on adsorbate nor on temperature. A corresponding-states principle appears to govern the interfacial behavior between water and any nonpolar compound that is sparingly soluble in water. A predictive method (without any adjustable parameter) is therefore available for estimating IFT between water and any nonpolar fluid, whether the fluid is in supercritical or in subcritical states. The method performs well when the adsorbate is sparingly soluble in water, but slightly overestimates IFTs when the adsorbate's solubility in water is significant (e.g., CO<sub>2</sub> and H<sub>2</sub>S). A similar behavior should also hold for interfaces involving a solid substrate.

## 1. Introduction

IFTs of fluid systems involving a water phase play an important role in many technical areas. For instance, the water/gas IFT controls the size of water droplets sprayed in a gas atmosphere through the dimensionless Weber number. Another quantity of utmost interest in hydrology and petroleum engineering is the capillary pressure between the water phase (usually the wetting phase) and the gas or oil (nonwetting) phase in a porous medium. This quantity, which is a function of water saturation in the porous medium, is proportional to the water/gas (or water/oil) IFT.

Several attempts have been made to build models to predict IFT against a water phase. The classical parachor approach, useful to evaluate liquid–vapor IFTs of hydrocarbon systems, is not appropriate for interfaces involving an aqueous phase. The correlation of Firoozabadi and Ramey<sup>1</sup> is based on the observation that the group  $IFT^{1/4} T_r^{0.3125} / \Delta\rho$  varies smoothly with  $\Delta\rho$ , the mass density difference between the aqueous and the nonaqueous (hydrocarbon) phase ( $T_r = T/T_c$ , where  $T_c$  is the critical temperature of the hydrocarbon compound, is the reduced temperature). This method is not appropriate in many cases, e.g., when the nonaqueous phase is liquid.<sup>2</sup> Models based on lattice theory and regular solution assumptions are of interest for water/liquid interfaces<sup>3</sup> but fail to describe water/gas IFTs at moderate and elevated pressures.<sup>4</sup>

Another more rigorous approach is the so-called gradient method. The “full” gradient method consists of determining the density profiles of the different compounds across the interface.<sup>5–10</sup> These profiles are such that they minimize the overall free energy

of the system and this minimum energy corresponds to the interfacial tension. In the systems of interest here, there are two such profiles, one for water,  $C_w$ , and the other for the nonaqueous compound,  $C_{nw}$ . The energy function consists of two parts: one is directly related to the free energy or equation of state (EoS) of the binary system and depends only on the local densities  $C_i$  ( $i = w$  and  $nw$ ), and the other part contains products of density gradients  $m_{ij}(dC_i/dZ)(dC_j/dZ)$ , where  $m_{ij}$  is the so-called influence coefficient between compounds  $i$  and  $j$  and  $Z$  the distance to the (planar) interface. The actual density profiles correspond to the minimum of this functional, which can be obtained by solving a set of coupled second-order differential equations. This set of equations is difficult to solve numerically when the crossed influence coefficients  $m_{ij}$  ( $i \neq j$ ) differ from the geometric average of the pure compound's influence coefficients  $\sqrt{m_i m_j}$  (in the case of a binary system there is only one such coefficient). Deviation from the geometric average requires the introduction of another coefficient  $\beta_{ij}$  (defined as  $m_{ij} = (1 - \beta_{ij})\sqrt{m_i m_j}$ ), which is usually adjusted to fit experimental IFT values.<sup>7,8</sup> Hence, the “full” gradient method cannot generally be considered as a predictive method.

Our purpose in this paper is to present a simple method, based on the standard Cahn gradient approach,<sup>11</sup> for predicting the interfacial properties between water and nonpolar fluids. This approach, summarized in next section, represents a considerable simplification over the “full” gradient method. In this approach, the interface is described by only one density profile (the water density profile is assumed to be step-like) and mutual solubilities of water and adsorbate are neglected (Figure 1). These assumptions are legitimate for nonpolar fluids when temperature is well

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below the critical temperature of water (647 K). The free energy term is much less complex than that required in the “full” gradient method. Here, we use the Peng–Robinson EoS (see the Appendix) that is well suited for nonpolar fluids and more generally for normal fluids. Normal fluids are defined as those fluids obeying an extended corresponding-states principle (which means that one parameter, here, the acentric factor, in addition to  $T_c$  and  $P_c$  is needed to describe thermodynamic properties). Normal fluids include most hydrocarbons and gases (e.g., Ar, N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>S, and etc.) and exclude molecules with specific (e.g., strongly polar or associating) interactions, such as alcohols, water, etc. Slightly polar compounds with significant solubility in water, such as H<sub>2</sub>S and CO<sub>2</sub>, are usually considered as normal fluids: their IFT with water will also be examined in this paper. [Strictly speaking, CO<sub>2</sub> is not a polar molecule (its dipolar moment is zero) but it is quadrupolar.]

The method introduced in this paper relies on the observation that the contact energy (an important element of Cahn theory) is a “universal” function of the adsorbate surface density when appropriate scaling variables are used. It extends Dobbs’ observation<sup>12</sup> for *n*-alkanes (from *n*-butane to *n*-octane) to any normal compound with limited solubility in water. This observation does not hold for normal compounds soluble in water, such as H<sub>2</sub>S and CO<sub>2</sub>.

This paper is structured as follows. The outline of standard Cahn gradient theory is presented in section 2. Two interfacial parameters are required in this approach: the adsorbate’s influence coefficient  $m$  and the water contact energy function  $\phi$ . In section 3, these two parameters are inferred respectively from experimental surface tension data of the pure adsorbate, and from Gibbs equation, i.e., from water/gas IFT isotherms of the water/adsorbate binary systems. We observe that the contact energy function is “universal” when proper scaling variables are used. In the last section, this universality is used to establish a method to predict interfacial properties between water and normal compounds sparingly soluble in water. Although our main focus is on IFTs, we argue that the approach introduced in this paper might be applicable to evaluate other interfacial properties such as adsorption and wetting behavior on water and also to systems involving a solid substrate instead of water.

## 2. Outline of the Standard Cahn Gradient Theory

In this approach, the aqueous phase is considered as an impenetrable substrate, onto which the nonaqueous molecules adsorb. This assumption is justified when these molecules have negligible solubility in water, which is the case of most of the normal compounds. Figure 1 schematically depicts the simplification introduced: instead of considering two density profiles  $C_w$  and  $C_{nw}$  (Figure 1a), only the one of the (nonaqueous) adsorbate  $C_{nw}$  is considered (Figure 1b). In the following sections, subscript nw is omitted from  $C_{nw}$ , hereafter denoted as  $C$ .

In the standard Cahn theory,<sup>11</sup> the free energy (per unit area) of the interface associated with an adsorbate density profile  $C(Z)$  is written as the functional form

$$\sigma = \phi(C_s) + \int_0^\infty \left[ \Delta f(C, C_0) + \frac{1}{2} m \left( \frac{dC}{dZ} \right)^2 \right] dZ \quad (1)$$

where

1.  $\phi$ , referred to as the contact energy function, sums up in an effective way interactions between substrate (i.e., water) and adsorbate. It is supposed sufficiently short-range to be considered as only dependent on  $C_s = \lim_{Z \rightarrow 0} C(Z) \approx C(Z=0)$ , the density

of adsorbate right at the substrate surface, which is now onward in the text called surface density.

2.  $\Delta f(C, C_0)$  is the (local) free energy density required to create a unit volume of adsorbate of density  $C$  from a reservoir with bulk density  $C_0 = C(+\infty)$ :  $\Delta f(C, C_0) = f(C) - f(C_0) - (C - C_0)\mu_0$ , where  $\mu_0 = (\partial f / \partial C)_{C_0}$  is the adsorbate chemical potential and the (Helmholtz) free energy density  $f$  of the adsorbate is directly related to the EoS, which we chose in this paper to be the Peng–Robinson EoS (see the Appendix),

3. The squared gradient term  $(1/2)m(dC/dZ)^2$ , where  $m$  is the adsorbate’s influence coefficient, represents the contribution of density inhomogeneities.

The actual density profile  $C(Z)$  is the one which minimizes the energy functional (1); that is, it satisfies the following Euler–Lagrange conditions:

$$\Delta f(C, C_0) = \frac{1}{2} m \left( \frac{dC}{dZ} \right)^2 \quad (2)$$

and

$$\frac{d\phi}{dC_s} = m \left( \frac{dC}{dZ} \right)_{Z=0} \quad (3)$$

In the situation of interest, adsorption onto water occurs; that is, the adsorbate density decreases with increasing distance  $Z$  from the substrate ( $dC/dZ < 0$ ), and therefore

$$\frac{dC}{dZ} = - \sqrt{\frac{2}{m} \Delta f(C, C_0)} \quad (2a)$$

By combining (2a) and (3), we obtain

$$\frac{d\phi(C_s)}{dC_s} + \sqrt{2m \Delta f(C_s, C_0)} = 0 \quad (4)$$

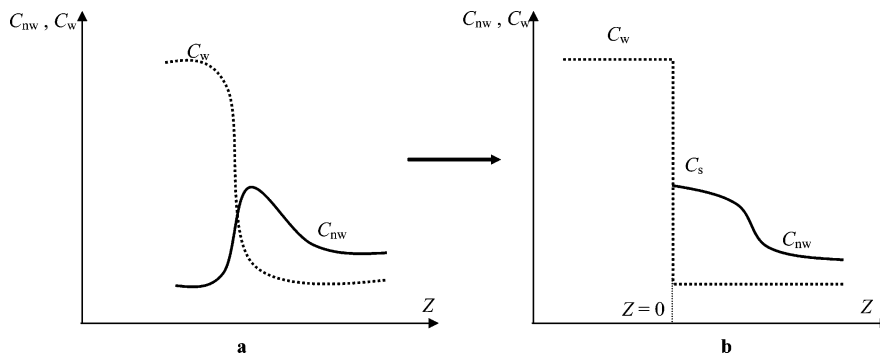
The actual surface density  $C_s$  corresponds to the physical root of (4), i.e., such that the interface free energy is minimum. The water/adsorbate IFT is obtained from (1), where  $C(Z)$  is the actual profile [given by (2) and (3)]

$$\sigma = \phi(C_s) + \sqrt{2m} \int_{C_0}^{C_s} \sqrt{[\Delta f(C, C_0)]} dC \quad (5)$$

This equation holds both at subcritical temperatures ( $T < T_c$ ) and at supercritical temperatures ( $T > T_c$ ), where  $T_c$  is the adsorbate’s critical temperature. In the subcritical regime,  $\sigma$  drops discontinuously from the water/vapor IFT  $\sigma_{wv}$  to the water/liquid IFT  $\sigma_{wl}$  when  $P$  reaches the adsorbate’s saturation pressure  $P_{sat}(T)$ , i.e., at three-phase coexistence between water (w), adsorbate-rich liquid (l), and vapor (v) phases. The discontinuity  $\sigma_{wv} - \sigma_{wl}$  is larger or equal to the adsorbate’s surface tension  $\sigma_{vl}$  (discussed in next section). The equilibrium spreading coefficient  $S = \sigma_{wv} - \sigma_{wl} - \sigma_{lv}$  characterizes the wetting behavior of liquid (l) on water (w): when  $S < 0$  the liquid partially wets the water substrate, forming droplets with contact angle  $\theta$  given by Young’s law ( $\cos \theta = 1 + S/\sigma_{lv}$ ), and when  $S = 0$ , there is complete wetting of the liquid on the substrate; that is, a film of macroscopic thickness forms between water and the vapor (v) phase. Within standard Cahn theory, the expression of  $S$  under partial wetting conditions is

$$S = - \int_{C_s}^{C'_s} \left[ \frac{d\phi}{dC} + \sqrt{2m \Delta f(C, C_0)} \right] dC \quad (6)$$

where the physical roots of (4)  $C_s$  and  $C'_s$  are the adsorbate’s surface densities at the water/vapor and water/liquid interfaces,



**Figure 1.** Simplification introduced by Cahn method: in the “full” gradient method, two density profiles are considered (a), whereas in Cahn approach only the density profile of the adsorbate  $C_{nw} = C$  is considered (b).  $Z = 0$  corresponds to the position of the (planar) water substrate.

respectively. The value of  $S$  at a given  $T$  and at  $P = P_{\text{sat}}(T)$  can be obtained from the contact energy function  $\phi$  and the free energy  $\Delta f$  by (i) finding the physical roots  $C_s$  and  $C'_s$  of (4) and then (ii) calculating the equilibrium spreading coefficient  $S$  by (6). Partial wetting usually occurs at low  $T$ ; upon increasing  $T$ , a transition from partial to complete wetting eventually occurs at some temperature  $T_w$  (below  $T_c$ ) corresponding to the vanishing of the equilibrium spreading coefficient ( $S = 0$ ). Within standard Cahn theory this transition is predicted to be first-order.<sup>13</sup>

The standard Cahn theory has several shortcomings: (i) it is of mean-field character and, therefore, fails to predict accurately interfacial properties near the adsorbate's critical point, (ii) it relies on a continuum description of density profiles, and therefore, it is inadequate at low pressure where abrupt density variations occur near the interface, and (iii) it takes only into account short-range interactions between substrate (water) and adsorbate. These shortcomings will be discussed in next sections.

Gibbs adsorption equation and the adsorption of the nonpolar adsorbate are expressed in next section, where we demonstrate how to infer interfacial parameters  $m$  and  $\phi$  from experimental data.

### 3. Interfacial Parameters $m$ and $\phi(C_s)$

#### 3.1. Influence Coefficient $m$ of the Nonaqueous Compound.

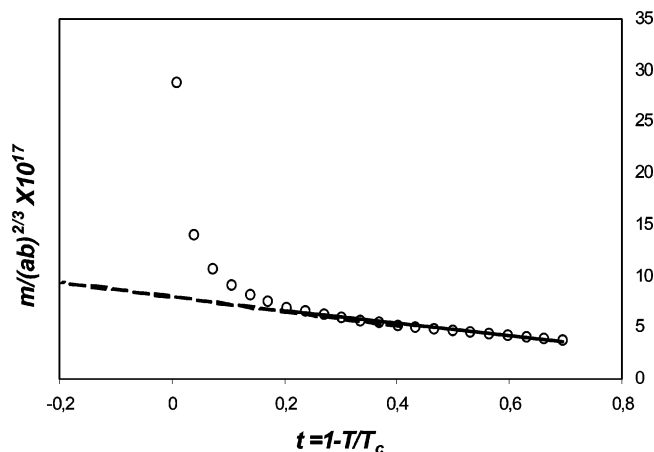
Following a common practice,<sup>5,8,14</sup> we adjusted the influence coefficient  $m$  to match the computed and experimental surface tensions of the adsorbate. Within gradient theory, the surface tension (or IFT between the adsorbate's coexisting liquid and vapor phases) is computed as follows:

$$\sigma_{lv} = \sqrt{2m} \int_{C_v}^{C_l} \sqrt{\Delta f(C, C_0)} dC \quad (7a)$$

where  $C_l$  and  $C_v$  are the densities of the liquid and vapor phases, respectively, and  $\Delta f(C, C_0)$  ( $C_0 = C_v$  or  $C_l$ ) is defined in previous section (see also the Appendix). (7a) is readily obtained by minimization of the energy functional of the liquid/vapor interface, i.e.,  $\sigma_{lv} = \int_{-\infty}^{+\infty} [\Delta f(C, C_0) + (1/2)m(dC/dZ)^2] dZ$ , with  $C_v = C(Z = -\infty)$  and  $C_l = C(Z = +\infty)$ . It is equivalent to the following expression:

$$\sqrt{m} = \frac{\sigma_{lv}}{\int_{C_v}^{C_l} \sqrt{2\Delta f(C, C_0)} dC} \quad (7b)$$

The influence coefficient  $m$  is therefore defined in the subcritical temperature range ( $T < T_c$ ) and is temperature-dependent. It is



**Figure 2.**  $m/ab^{2/3}$  values [calculated from surface tension data and using (7b)] of ethane at different reduced temperatures  $t = 1 - T/T_c$  (circles). In the subcritical region ( $t \geq 0.2$ ),  $m/ab^{2/3}$  varies linearly with  $t$ . This linear behavior (solid line) is extrapolated (dashed line) to give values of  $m/ab^{2/3}$  in the near-critical and supercritical regions.

indeed related to the EoS and its parameters. Our purpose here is to determine  $m(T)$  for different compounds and at conditions of interest in this work (see section 3.2), which include supercritical temperature conditions for some adsorbates ( $T > T_c$ ). In such cases when  $m(T)$  cannot indeed be calculated using (7b), we adopt the approach used in the “full” gradient method for multicomponent mixtures: the values of  $m(T)$  is obtained by extrapolating the values of  $m(T)$  calculated in the subcritical region.<sup>6,15</sup> We also use this method for determining  $m(T)$  in the near-critical region ( $T \approx T_c$ ) where the strict application of (7b) leads to diverging values (see Figure 2): this divergence manifests the failure of Cahn theory and of the PR EoS to describe near-critical states (see the discussion in the end of this subsection).

We extrapolate the dimensionless quantity  $m(T)/ab^{2/3}$  ( $a$  and  $b$  are the EoS parameters, see the Appendix) from the subcritical to the near-critical and supercritical temperature regions (Figure 2 illustrates the case of ethane). The linear regression parameters  $A$  and  $B$  are defined as follows:

$$\frac{m}{ab^{2/3}} = A(1 - T_r) + B \quad (8)$$

Table 2 lists the values of the regression parameters  $A$  and  $B$  of nine light compounds including argon, nitrogen, CO<sub>2</sub>, H<sub>2</sub>S, and

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**Table 1. Constants  $A$  and  $B$  (eq 8) Inferred from Surface Tension Data Taken from ref 18**

compound	$A (\times 10^{17})$	$B (\times 10^{17})$
methane	-8.89	9.6
ethane	-7.25	8.44
propane	-5.71	7.75
<i>i</i> -butane	-6.06	7.81
<i>n</i> -butane	-4.92	7.09
nitrogen	-17.02	10.41
argon	-7.40	8.94
carbon dioxide	-35.5	12.8
hydrogen sulfide	-26.3	12.3

the lighter alkanes (from methane to butane).  $T_c$ ,  $P_c$ , and  $\omega$  values are taken from ref 16.

For *n*-pentane and higher *n*-alkanes, we used the Carey and Scriven<sup>14</sup> expression

$$m = 3.78 \times 10^{-17} ab^{2/3} + 7.25 \times 10^{-20} \quad (9)$$

More quantitatively, the observed divergence of  $m(T)$  near  $T_c$  ( $t \rightarrow 0$ ) is the result of the denominator in (7b) (which is proportional to the mean-field expression for surface tension) that varies like  $t^{3/2}$ , whereas experimental surface tension [i.e., the numerator in (7b)] varies like  $t^\mu$ , where the scaling exponent  $\mu = 1.26$ .<sup>17</sup>

**3.2. Water Contact Energy Function.** Within Cahn theory, the contact energy function  $\phi(C_s)$  and IFT with water are related at a given temperature by (4) and (5). The following expression, obtained by differentiation of (5) with respect to  $C_0$ ,<sup>9</sup> is more convenient to use than (5) because  $\phi(C_s)$  no longer appears

$$\frac{d\sigma}{dC_0} = -\sqrt{\frac{m}{2}} \left( \frac{\partial^2 f}{\partial C^2} \right)_{C_0} \int_{C_0}^{C_s} \frac{C - C_0}{\sqrt{\Delta f(C, C_0)}} dC \quad (T \text{ constant}) \quad (10)$$

Thus,  $C_s$  can be determined from water/gas IFT data, and then  $\phi(C_s)$  is obtained from (5).

The above expression is nothing but Gibbs adsorption equation  $\Gamma = (\partial\sigma/\partial\mu)_T$ , where  $\mu$  is the chemical potential and  $\Gamma$  the adsorption of the nonpolar compound

$$\Gamma = \int_0^{+\infty} (C(Z) - C_0) dZ \quad (11)$$

In (11)  $dZ$  can be replaced by

$$-\sqrt{\frac{m}{2}} \int_{C_0}^{C_s} \frac{dC}{\sqrt{\Delta f(C, C_0)}}$$

(see 2a), which leads to

$$\Gamma = \sqrt{\frac{m}{2}} \int_{C_0}^{C_s} \frac{(C - C_0)}{\sqrt{\Delta f(C, C_0)}} dC \quad (12)$$

(10) and (12) are two equivalent forms of Gibbs equation. (10) is of interest for water/fluid systems investigated here, in which the most accessible interfacial property is IFT. (12) is of more interest for solid/fluid systems, in which adsorption isotherms  $\Gamma(P)$  are often available. These two equations can be used to establish the contact energy function  $\phi(C_s)$  from an IFT isotherm (10) or from an adsorption isotherm (12). In the first case,

**Table 2. Experimental Water/Gas IFT Data at Ambient Temperature Used in the Determination of the Contact Energy Function<sup>a</sup>**

system	$T$ (°C)	$P$ (bar)	%AAD	%MAD	ref
water/CH <sub>4</sub>	25	0–74	0.14	0.36	19
	25	150–300	1.69	3.52	20
water/C <sub>2</sub> H <sub>6</sub>	25	0–40	2.14	4.38	19
water/C <sub>3</sub> H <sub>8</sub>	25	0–9	2.12	4.58	19
water/ <i>n</i> C <sub>4</sub> H <sub>10</sub>	15	0–2.1	0.42	1.43	19
water/ <i>i</i> C <sub>4</sub> H <sub>10</sub>	25	0–2.5	0.49	2.05	19
water/ <i>n</i> C <sub>5</sub> H <sub>12</sub>	15	0–0.46	0.2	0.3	21
water/ <i>n</i> C <sub>6</sub> H <sub>14</sub>	15	0–0.13	0.33	0.99	21
water/Ar	25	0–80	0.12	0.29	22
water/N <sub>2</sub>	25	0–80	0.18	0.54	22
water/CO <sub>2</sub>	25	0–59	5.55	8.74	19
water/H <sub>2</sub> S	25	0–16	10.24	21.26	23, 24

<sup>a</sup> Comparison between calculated IFT values and experimental data.

measurements are usually presented in terms of surface pressure isotherms  $\Pi(P) = \sigma_0 - \sigma$ , where  $\sigma$  is the IFT at pressure  $P$  and  $\sigma_0$  is the surface tension of pure water at the same temperature. For a given  $P$  (corresponding to a bulk density  $C_0$  determined from the EoS),  $C_s$  is first calculated from (10), where  $d\sigma/dC_0$  is written as  $-d\Pi/dC_0 = (-d\Pi/dP)(dP/dC_0)$ , where  $d\Pi/dP$  is directly related to surface pressure data, and  $dP/dC_0$  is related to the EoS; then the contact energy function  $\phi$  for that particular value of  $C_s$  is determined using (5), i.e.

$$\phi(C_s) - \sigma_0 = -\Pi - \sqrt{2m} \int_{C_0}^{C_s} \sqrt{\Delta f(C, C_0)} dC \quad (13)$$

Here, it is clear that for vanishing pressure (or, more precisely, when  $P$  approaches the water saturation pressure)  $C_s \rightarrow 0$  and  $\phi \rightarrow \sigma_0$ , i.e.,  $\phi(C_s \rightarrow 0) = \sigma_0$ .

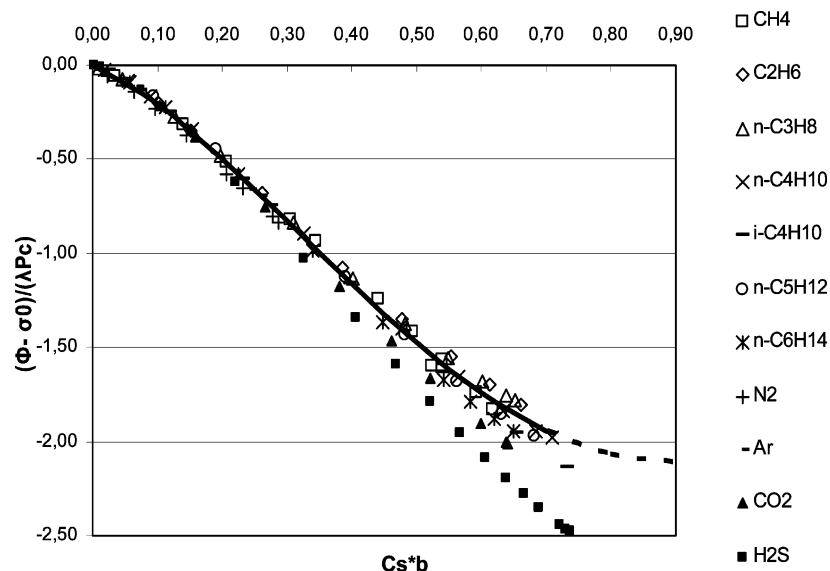
In refs 12 and 9, the water contact energy function was determined by this procedure for the series of intermediate *n*-alkanes from *n*-butane to *n*-octane using available water/*n*-alkanes IFT values at near-ambient temperature. Dobbs<sup>12</sup> observed that, if appropriate energy and density scaling variables are utilized, the reduced contact energy is a unique function of reduced density for all *n*-alkanes investigated. The scaling variables are  $1/b$  for  $C_s$  and  $\lambda P_c$  for the contact energy, where the length scale  $\lambda = (m/b^2 P_c)^{1/2}$  is of the order of 3–4 nanometers.<sup>12</sup> These scaling variables appear naturally when rewriting the EoS and Cahn's expressions provided in section 2 (see the Appendix). We examined whether Dobbs' observation on intermediate *n*-alkanes holds for other normal compounds. If it turns out to be the case, then we have access to a simple, accurate and fully predictive method for the interfacial properties of these systems.

Using the available water/gas IFTs (see Table 2 for the detailed information), (10) and (13) we have determined the water contact energy  $\phi(C_s)$  of all of the compounds considered in section 3.1: argon, nitrogen, lower alkanes up to hexane, carbon dioxide, and hydrogen sulfide. The influence coefficients obtained in section 3.1 are used in this calculation.

Results of this analysis presented in Figure 3 show that the reduced contact energy functions  $\Phi = (\phi - \sigma_0)/\lambda P_c$  of the various compounds are barely distinguishable when expressed as a function of  $bC_s$ , except in the case of CO<sub>2</sub> and H<sub>2</sub>S. For the latter two compounds the reduced contact energy is lower, especially in the case of H<sub>2</sub>S and at high  $C_s$ . However, these two compounds are considerably more soluble in water than the other compounds and therefore they do not fulfill an important requirement of Cahn theory. We could fit all points in Figure 3 except those for

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**Figure 3.** Reduced contact energy  $\Phi = (\phi - \sigma_0)/\lambda P_c$  as a function of  $bC_s$  for various normal compounds inferred from experimental water/gas IFTs at 25 °C (methane, ethane, propane, i-butane, nitrogen, argon, CO<sub>2</sub>, and H<sub>2</sub>S) and at 15 °C (*n*-butane, *n*-pentane, and *n*-hexane). (Solid line) Fourth-order polynomial (14) fit in a range  $0 < bC_s < 0.7$ ; (dashed line) extrapolation of polynomial (14) in a range  $bC_s > 0.7$ .

CO<sub>2</sub> and H<sub>2</sub>S to the following fourth-order polynomial over the interval  $0 < bC_s < 0.7$ .

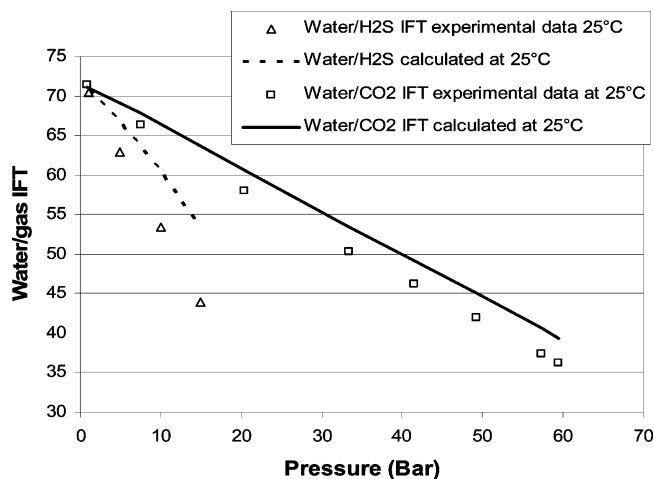
$$\Phi(bC_s) = \frac{\phi(C_s) - \sigma_0}{\lambda P_c} = -2.08(bC_s)^4 + 7.61(bC_s)^3 - 6.01(bC_s)^2 - 1.58(bC_s) \quad (14)$$

The points in Figure 3 could also be correctly fitted with a second-order or a third-order polynomial over this interval. However, the extrapolation of these polynomials in the high surface density range ( $bC_s > 0.7$ ) differ significantly from the extrapolation of (14) (depicted in Figure 3), leading to incorrect predictions of water/liquid IFTs, as discussed in next section.

For slightly volatile compounds (*n*-pentane and *n*-hexane), the correctness of experimental surface pressure values  $\Pi(P)$  taken from ref 21 has been questioned.<sup>25</sup> In fact these values are small (in the range of 1 mN/m or less) for under-saturated vapors and difficult to measure. We performed a sensitivity analysis to study the impact of a variation of  $\Pi(P)$  (up to 30%) on calculated  $\Phi(C_s)$  values: we observed a negligible effect, as it might be expected from inspection of (13); the right-hand-side of this equation is dominated by the integral term for small  $\Pi(P)$  values. For these compounds, the validation of the proposed polynomial (14) also stems from a comparison between calculated and measured water/liquid IFTs, as the latter are known precisely (see next section).

The polynomial (14) together with (4) and (5) provides calculated water/gas IFTs at ambient temperature very close to measured values, except in the case of CO<sub>2</sub> and H<sub>2</sub>S (see Figure 4). The differences between calculated and measured values are reported in Table 2 for each compound in terms of % average and maximum absolute deviations (%AAD and %MAD). %AAD is the percentage average absolute deviation, defined as: %AAD =  $(1/N) \sum_i (|\sigma_i^{\text{exp}} - \sigma_i^{\text{calc}}|/\sigma_i^{\text{exp}}) \times 100$ , where  $N$  is the number of data points (labeled by  $i$ ) and  $\sigma_i^{\text{exp}}$  and  $\sigma_i^{\text{calc}}$  are the experimental and calculated IFT at same temperature and pressure. %MAD is the percentage maximum absolute deviation, defined as %MAD =  $\text{Max}_i [(|\sigma_i^{\text{exp}} - \sigma_i^{\text{calc}}|/\sigma_i^{\text{exp}}) \times 100]$ .

Concerning the temperature dependence of the reduced contact energy  $\Phi = (\phi - \sigma_0)/\lambda P_c$ , we note that the range of temperatures

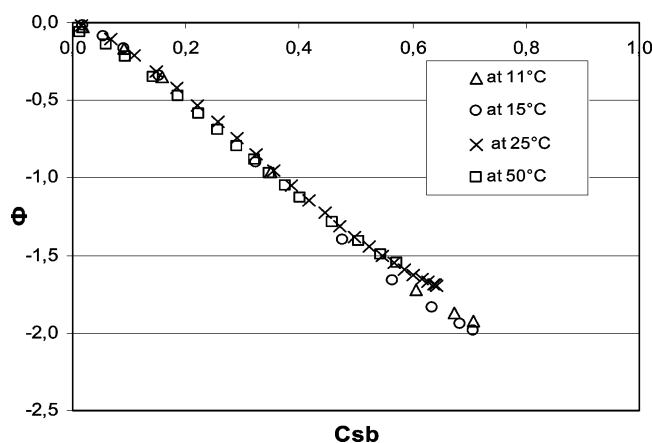


**Figure 4.** Water/CO<sub>2</sub> and water/H<sub>2</sub>S IFTs at 25 °C: comparison between calculated values and experimental data. Model overestimates IFTs and the overestimation is more pronounced at the highest pressures (~10% at 59 bar in the case of CO<sub>2</sub> and ~20% at 15 bar in the case of H<sub>2</sub>S).

of the experimental isotherms considered in Figure 3 is very large, i.e., from  $T_r \sim 2$  for argon to  $T_r \sim 0.5$  for *n*-hexane. This suggests that  $\Phi$  depends negligibly on temperature. An example of this negligible dependence is provided in the case of *n*-butane in Figure 5, where the reduced contact energy functions  $\Phi$  are plotted at various temperatures corresponding to different isotherms taken from the literature.<sup>19</sup> Other compounds with which we possess IFT isotherms at different temperatures displayed the same negligible dependence of the contact energy function on temperature (data not shown). Using expression (14) together with (4) and (5), we calculated the IFTs of the systems for which measured IFT data are available at different temperatures. Table 3 provides a comparison of calculated and measured values in terms of the % AAD and MAD: the agreement between both sets of values is very good.

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**Figure 5.**  $\Phi = (\phi - \sigma_0)/\lambda P_c$  vs  $bC_s$  for *n*-butane at  $T = 11$  (triangles), 15 (circles), 25 (crosses), and 50 °C (squares), inferred from the experimental IFT data of ref 19.

**Table 3. Water/Gas IFT at Various Temperatures<sup>a</sup>**

system	$T$ (°C)	$P$ (bar)	%AAD	%MAD	ref
water/CH <sub>4</sub>	2	0–64	0.77	1.51	19
	50	4–66	0.99	1.39	19
	80	10–300	4.15	6.08	20
	100	10–300	6.12	10.61	20
water/C <sub>2</sub> H <sub>6</sub>	48	0–37	2.61	4.1	19
water/C <sub>3</sub> H <sub>8</sub>	10	0–6	2.12	4.58	19
	50	0–9	2.15	3.51	
water/ <i>n</i> C <sub>4</sub> H <sub>10</sub>	11	0–1	0.42	1.43	19
	25	0–0.9	1.16	2.52	
	50	0–2	1.64	2.17	
water/ <i>i</i> C <sub>4</sub> H <sub>10</sub>	11.2	0–1.8	0.49	2.05	19
	49.1	0–2.9	1.03	1.44	
water/CO <sub>2</sub>	45	1–57	0.83	1.91	19
water/H <sub>2</sub> S	50	1–30	8.74	20.63	
	70	1–30	2.88	6.78	23
	110	1–30	1.89	2.45	

<sup>a</sup> Comparison between experimental values and calculated values using eqs 14, 4, and 5.

**Table 4. Water/Liquid IFT at Various Temperatures<sup>a</sup>**

system	$T$ (°C)	$P$ (bar)	%AAD	%MAD	ref
water/C <sub>3</sub> H <sub>8</sub>	25	20–400	2.56	4.67	29
water/ <i>n</i> C <sub>6</sub> H <sub>14</sub>	25	37–289	0.85	1.83	30
	25	1–200	1.11	1.8	29
	50	1–600	2.86	6	29
water/ <i>n</i> C <sub>8</sub> H <sub>18</sub>	25	40–284	4.9	6.09	30
	50	40–289	3.35	4.41	
water/ <i>n</i> C <sub>10</sub> H <sub>22</sub>	25	43–282	1.0	1.94	30
	50	39–278	3.34	4.32	

<sup>a</sup> Comparison between experimental values and calculated values using eqs 14, 4, and 5.

#### 4. Discussion and Perspectives

In the preceding section, the two interfacial parameters required for the implementation of the standard Cahn theory were determined from a set of experimental surface and interfacial tension data of various systems. The first parameter is the influence coefficient  $m$  of the (pure) nonpolar adsorbate, which was determined by matching experimental surface tension data of pure fluid and the surface tension calculated within gradient theory (eq 7). The second parameter is the water contact energy function  $\phi(C_s)$ , which was obtained by matching experimental and calculated water/adsorbate IFTs [using (5) and (10), where the latter is nothing but Gibbs equation]. Both parameters were determined using an extended corresponding-states description of free energy and bulk properties (using the Peng–Robinson EoS, see the Appendix). We observed that the water contact

energy, when scaled by appropriate variables, is a unique function of adsorbate surface density and is not only independent of the nonpolar adsorbate but also of temperature. This observation holds for all nonpolar adsorbates which have very limited solubility in water.

This empirical observation would deserve some theoretical justification. However, derivation of the surface energy in terms of intermolecular potentials and other fluid or substrate parameters is a difficult task.<sup>26</sup> In a very recent work, Weiss<sup>27</sup> established a relationship between the contact energy function  $\phi$  and the Hamaker constant of the adsorbate film and its two-dimensional EoS describing surface pressure as a function of adsorbate's surface density.

From a practical point of view, this apparent “universality” of the water contact energy allows us to propose a simple procedure for predicting IFTs between water and a normal compound sparingly soluble in water. It consists of two steps:

(i) In the first step, the adsorbate's bulk density  $C_0$  at  $T$  and  $P$  is obtained using the PR EoS (see the Appendix), then (4) is solved for its physical root  $C_s$ . The adsorbate's influence coefficient  $m$  at given  $T$  is determined (or extrapolated) using surface tension data (see section 3.1).

(ii) In the second step, IFT is calculated by using (5).

This procedure is directly applicable to predict IFT of systems in which the adsorbate is either in supercritical [ $T > T_c$ ] or in gaseous (subcritical) [ $T < T_c$  and  $P < P_{\text{sat}}(T)$ ] state. In order to calculate IFTs when the adsorbate is liquid [ $T < T_c$  and  $P > P_{\text{sat}}(T)$ ], an expression of  $\Phi$  is required for surface densities higher than the range ( $bC_s > 0.7$ ). The most natural procedure consists in extrapolating the polynomials obtained in the surface density range ( $0 < bC_s < 0.7$ ) from water/gas IFTs (see previous section). We found that the use of the fourth-order polynomial (14) in the entire surface density interval ( $0 < bC_s < 1$ ) leads to more accurate predictions of water/liquid IFTs than the use of lower order polynomials. In fact, only the fourth-order polynomial (14) is almost constant in the region  $bC_s > 0.7$  (see Figure 3) and is able to reproduce the observed slight pressure dependence of water/liquid IFT when the nonpolar fluid is slightly volatile (Table 4).

In<sup>9,12,28</sup> the derivative of  $\Phi$  with respect to adsorbate surface density was extrapolated linearly in the region  $bC_s > 0.7$ . We calculated IFT values using this type of extrapolation and found that the calculated values were 10–15% lower than experimental values.

In refs 9, 12, and 28 the primary interest was in the interfacial properties of three-phase systems [ $P = P_{\text{sat}}(T)$ ], in which the water substrate coexists with two nonaqueous liquid and vapor phases. The properties of interest were the wetting behavior<sup>28</sup> and the tension of the three-phase line.<sup>12</sup> We calculated within standard Cahn theory the wetting transition temperature  $T_w$  [corresponding to the vanishing of the integral (6)] of *n*-pentane and *n*-hexane on water using expression (14) for  $\Phi$ . We obtained  $T_w/T_c = 0.53$  and 0.55 for *n*-pentane and *n*-hexane, respectively, which agree to within 2–3% with the published values.<sup>9,28</sup> These values are below the experimental transition temperatures, 0.64

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and 0.68 respectively.<sup>31</sup> We conclude that the proposed extrapolation (14) in the range  $0.7 < bC_s < 1$  allows improved prediction of water-liquid IFT compared to the extrapolations proposed in refs 9, 12, and 28; at the same time the predicted wetting transition temperatures of intermediate *n*-alkanes on water remains comparable.

It is worth mentioning here that slightly better predictions of wetting transition temperatures is obtained within another variant of the standard Cahn theory, in which the contact energy function is a non-universal second-order polynomial of  $C_s$  adjusted to reproduce the initial spreading coefficient  $S_0$ .<sup>32</sup>  $S_0$  is defined similarly to the equilibrium spreading coefficient  $S$  introduced in section 2, but with the water/gas IFT  $\sigma_{wg}$  replaced by the pure water surface tension  $\sigma_0$ . It thus characterizes the initial spreading of a drop of the nonpolar liquid deposited on water. This approach<sup>32</sup> is used with slightly volatile compounds and has not been tested for water/gas IFT prediction.

There are several shortcomings and possible extensions of the proposed method, which are as follows [(i), (iii), and (iv) were also briefly mentioned in section (2)].

(i) The method is mean-field in character and therefore is inadequate to describe water/fluid interfaces near the fluid's critical point (e.g., at  $T$  just above  $T_c$  and at a fluid density close to the critical density). In this situation, referred to as critical adsorption, interfacial quantities such as adsorption and interfacial tension are characterized by scaling laws with universal exponents<sup>17</sup> that differ from the mean-field exponents obtained within Cahn theory.<sup>33</sup>

(ii) When the solubility of the nonaqueous compound (adsorbate) in water is not negligible, as in the case of  $\text{CO}_2$  and  $\text{H}_2\text{S}$ , a significant overestimation (by around 10–15%) of water/gas IFTs is observed while using the “universal” contact energy function (14) in the calculation; water/liquid IFTs are overestimated as well. We observed that deviations between measured and calculated values are correlated with compound's solubility in water: in the case of  $\text{CO}_2$  and  $\text{H}_2\text{S}$  the deviation is maximum at lowest temperature, when solubility is maximum, and then decreases with increase in temperature. Thus, this shortcoming might be overcome by using an energy function lower than (14), e.g., by multiplying it with a factor (larger than unity) increasing with compound's solubility in water.

(iii) The standard Cahn approach used here does not describe correctly interfacial states at low pressure. In this so-called Henry's regime, IFT and surface adsorption vary linearly with pressure,<sup>34,35</sup> which the standard Cahn theory is unable to reflect.<sup>12</sup> This is due to the fact that Cahn theory is a continuum model unable to account for the abrupt density variation occurring near the substrate at low pressure. Dobbs<sup>12</sup> proposed a modification of the standard Cahn theory in which the adsorbate density is described in terms of a discrete layer near the substrate, while keeping the continuum profile beyond this layer. The layer thickness is the new parameter in this modified Cahn theory: the experimental values  $T_{rw} = 0.64$  and  $0.68$  for water/pentane and water/hexane, respectively, can be matched by using a thickness in the range of  $4 \text{ \AA}$ , consistent with the thickness of

alkane chains lying flat on water.<sup>28</sup> The application of the modified Cahn theory to other normal compounds than the intermediate *n*-alkanes should not be a difficult task, but the question of the layer thickness value should be answered first.

(iv) The standard Cahn approach takes into account only short-range interactions between water and adsorbate (through the contact energy function that depends only on the local adsorbate density  $C_s$ ). Although long-range (van der Waals) interactions have a negligible effect on interfacial energies (the main interest of this paper), it is worth mentioning here that they give rise to a complex wetting behavior, that has been thoroughly studied (both experimentally and theoretically) in the case of intermediate *n*-alkanes (see ref 13 for a review). The transition predicted within standard Cahn theory (as calculated above for intermediate *n*-alkanes), in which partial wetting prevails at  $T < T_w$  and complete wetting at  $T > T_w$ , is slightly modified by the presence of antagonistic long-range forces, that prevent the wetting film to grow to macroscopic thickness above  $T_w$  (this thickness is said to be mesoscopic). The Hamaker constant of this film is in fact positive in a temperature interval  $T_w < T < T_{wc}$ , where  $T_{wc}$  corresponds to the vanishing and change in sign of this constant. At  $T_{wc}$  another wetting transition takes place between a mesoscopic film and a macroscopic film, which is continuous and reversible in nature. This sequence of (three) different wetting states and (two) transitions, observed with intermediate alkanes, is understood theoretically<sup>36</sup> from an interface energy functional (1) in which a contribution of long-range forces is incorporated.<sup>37</sup> A more complete and precise description of three-phase interfacial properties emerges, including line tension, contact angles as well as the location and features of both wetting transitions.<sup>27,38,39</sup> It would be interesting in the future to examine whether long-range interactions obey a corresponding-states description as well, and whether the complex wetting behavior encountered for *n*-alkanes on water also holds for other insoluble normal compounds.

We showed that IFT between water and a nonpolar (normal) compound can be predicted within a corresponding-states approach, in which only the compound's surface tension and critical parameters  $T_c$ ,  $P_c$ , and acentric factor  $\omega$  are needed. In a forthcoming work, we will extend this approach to systems in which the adsorbate is not a pure compound but a mixture, such as a petroleum reservoir (gas or oil) fluid.

The same unified framework could be used to describe not only the tensions in both supercritical and subcritical regimes (which was the main subject of this paper), but also the density profile (by solving 2a), the interface thickness and adsorbed quantity (11) as well as three phase properties such as wetting behavior, contact angles, and line tension. We expect that the same corresponding-states behavior should also hold for normal compounds when the substrate is a solid (instead of an aqueous phase) but subject to the condition that there is no specific interaction between substrate and adsorbate. In this respect it would be interesting to examine adsorption isotherms of various normal compounds on a given solid substrate in the light of the corresponding-states and gradient approach proposed in this paper.

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**Supporting Information Available:** Calculated and experimental IFT values are provided for interested readers. This information is available free of charge via the Internet at <http://pubs.acs.org>.

### Appendix

The Peng–Robinson (PR) equation of state (EoS), which accurately predicts the saturation curve of normal compounds, is a cubic equation of the van der Waals type relating pressure  $P$ , temperature  $T$ , and molar density  $C$

$$P = \frac{CRT}{1 - bC} - \frac{aC^2}{1 + bC(2 - bC)} \quad (\text{A1})$$

where  $a$ ,  $b$ , and  $R$  are the interaction parameter, excluded volume, and gas constant respectively. For a pure compound, the interaction parameter  $a$  is temperature-dependent

$$a(T) = a(T_c)\alpha(T_r) \quad (\text{A2})$$

where  $a(T_c) = a_c$  is (like  $b$ ) related to the compound's critical temperature  $T_c$  and pressure  $P_c$  [see below (A5) and (A6)] and  $\alpha(T_r) = [1 + K(1 - T_r^{1/2})]^2$  where the constant  $K$  depends only on the acentric factor  $\omega = -1 - \ln[P_{\text{sat}}(T_r = 0.7)]$  as follows<sup>40</sup>

$$K = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (\omega < 0.49) \quad (\text{A3})$$

$$K = 0.379642 + 1.48503\omega - 0.164423\omega^2 + 0.016666\omega^3 \quad (\omega \geq 0.49) \quad (\text{A4})$$

The values of  $a_c$  and  $b$  are obtained from the two critical point conditions  $(\partial P/\partial C)_T = (\partial^2 P/\partial C^2)_T = 0$

$$a_c = \Omega_a \frac{(RT_c)^2}{P_c} \quad (\text{A5})$$

$$b = \Omega_b \frac{RT_c}{P_c} \quad (\text{A6})$$

where  $\Omega_a$  and  $\Omega_b$  are equal to 0.457235 and 0.077796 respectively for the PR EoS.

The (Helmholtz) free energy density  $f = A/V$  (where  $V$  is total volume) is deduced from  $P$  as follows:

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$$A = \int_V^\infty \left( P - \frac{nRT}{V} \right) dV - nRT \ln(V/nRT) \quad (\text{A7})$$

then  $\mu = (\partial A/\partial n)_T = (\partial f/\partial C)_T$  and finally  $\Delta f(C, C_0) = f(C) - f(C_0) - (C - C_0)\mu_0$  are readily obtained<sup>5,9</sup> as a function of molar density  $C = n/V$ , where  $n$  is the number of moles of the adsorbate. In (A7) we have omitted a linear term in  $T$  and  $C$  which cancels out in the final expression of  $\Delta f(C, C_0)$ .<sup>5,9</sup>

In (A1), the natural dimensionless density variable is  $x = bC = C/C_{\text{max}}$ , where  $C_{\text{max}} = 1/b$  is the maximum molar density (reached at infinitely high pressure):  $x$  ranges between 0 and 1 and is called the compacity. Thus reduced pressure  $P_r = P/P_c$  is a function of reduced temperature  $T_r$  and  $x$  only

$$\frac{P}{P_c} = \frac{xT_r}{\Omega_a(1-x)} - \frac{\Omega_a a(T_r)^2}{\Omega_b^2 [1 + x(2-x)]} \quad (\text{A8})$$

Similarly  $f$  scaled by  $P_c$  is a dimensionless function of  $x$  and  $T_r$ .

By rewriting the differential eq 2 with these dimensionless variables, a natural length scale variable  $\lambda = (m/b^2 P_c)^{1/2}$  appears

$$\frac{dx}{d(Z/\lambda)} = -\sqrt{2\delta f(x, x_0, T_r)},$$

$$\text{where } \delta f = \Delta f/P_c, x = bC, x_0 = bC_0 \quad (\text{A9})$$

Using this length scale, (4) can then be rewritten as follows:

$$\frac{d\phi}{dx_s} + \lambda P_c \sqrt{2\delta f(x_s, x_0, T_r)} = 0 (x_s = bC_s) \quad (\text{A10})$$

where  $\lambda P_c$  is a natural scaling parameter of the contact energy function  $\phi$ . IFTs and contact energy functions in eqs 5, 6, and 9 can likewise be scaled by  $\lambda P_c$ . Finally, the adsorption  $\Gamma$  (11) in terms of  $x$  and  $T_r$  can be written as

$$\Gamma = \frac{\lambda}{b} \int_{x_0}^{x_s} \frac{(x - x_0)}{\sqrt{2\delta f(x, x_0, T_r)}} dx \quad (\text{A11})$$

Equation 6 giving the equilibrium spreading coefficient on water of an adsorbate liquid in equilibrium with its vapor can also be written in terms of reduced variables

$$\frac{S}{\lambda P_c} = - \int_{x_s}^{x'_s} \left[ \frac{d\Phi}{dx} + \sqrt{2\delta f(x, x_0, T_r)} \right] dx \quad (\text{A12})$$

where  $x_s$  and  $x'_s$  are the physical roots of (A10). It is then clear that the integral on the right-hand side of (A15) vanishes at a value of the reduced temperature  $T_{\text{rw}} = T_w/T_c$  that depends only on  $\omega$ .

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