

Line Tension of *n*-Alkanes on Water from a Cahn-Type Theory

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We apply the phenomenological theory of Cahn, generalized to include van der Waals forces, to the wetting of *n*-alkanes on water, deriving an interface potential from which the line tension is calculated. For the *n*-alkanes considered (butane to octane) the typical magnitude of the line tension is of the order of 10^{-12} N, rising to a maximum of $+5 \times 10^{-12}$ N in the vicinity of a first-order wetting transition or a transition between thin and thick wetting films. Close to critical wetting transitions, the line tension is negative and also of the order of 10^{-12} N, but it vanishes at wetting. We also calculate the boundary tension for various thin–thick transitions that extend into the one-phase region of the bulk phase diagram, such as prewetting, which has the same order of magnitude.

1. Introduction

The wetting of an interface between two bulk phases by a third coexisting phase can be investigated by measuring either the contact angle of droplets of the third phase or the thickness of adsorbed films of the third phase at the interface.^{1–3} For situations of partial wetting, droplets describe a finite contact angle and the adsorbed films are of finite, usually molecular, thickness. For complete wetting, the contact angle vanishes and droplets placed at the interface spread over the surface, forming adsorbed films of indefinite thickness.

For the case of an *n*-alkane spreading over the surface of water in an atmosphere saturated with the alkane vapor, experiments based on visual inspection of droplets have determined that pentane and higher homologues are partially wetting at 24 °C.⁴ However pentane is unusual among these in that the adsorbed film, approximately 50 Å thick, coexisting with the droplets is rather thicker than the molecularly thin film that forms for higher homologues. Recent ellipsometry measurements for pentane have shown that as the temperature increases, the film thickens continuously and there is a critical wetting transition between partial and complete wetting at 53 °C.⁵ Larger *n*-alkanes are thought to remain partially wetting up to much higher temperatures.

The continuous nature of the wetting transition for pentane indicates that the Hamaker constant, which is a measure of the tendency of the long-range (van der Waals) component of the interactions between water and alkane to prevent the alkane layer from growing, decreases with increasing temperature and passes through zero at the wetting temperature. However, the unusual thickness of the wetting film at room temperature cannot be explained purely in terms of van der Waals forces. Short-range forces at the interface with the water also play a significant role in determining the wetting properties of *n*-alkanes. In the case of pentane, while long-range forces

prevent wetting below the wetting temperature, calculations of the short-range forces suggest that these favor wetting above –30 °C.⁶ An adsorbed film that is thick yet finite results from this competition. For the higher homologues, it is thought that both short- and long-range forces disfavor wetting up to temperatures too close to the boiling point of water to be experimentally accessible, so that the adsorbed film is always of molecular thickness.

Now, in an extraordinary experiment, it has been shown recently that it is possible to tune the interactions in the hexane system so that a wetting transition *does* take place at an accessible temperature.⁷ Adding salt to the water reduces the Hamaker constant so that it reaches zero somewhat below 100 °C, and a continuous wetting transition is observed. Even more remarkable, a second transition occurs in the adsorbed film below the wetting temperature, where the film thickness jumps discontinuously from being molecularly thick to about 100 Å thick.⁷ This occurs when the short-range forces change from disfavoring to favoring wetting, while long-range forces still prevent wetting.⁸

The general picture of wetting in *n*-alkanes can be summarized briefly. At low temperatures short-range and long-range forces disfavor wetting, but both change to favoring wetting at higher temperatures. The action of the short-range forces tends to result in discontinuous jumps in the wetting film thickness (first-order transitions),⁶ while the long-range forces produce continuous behavior since the subdominant terms in the expansion of the long-range forces already favor wetting. The nature of the wetting transition that occurs is determined by the relative temperatures at which the two types of force change to favoring wetting.

If the short-range forces change to favoring wetting at lower temperatures than the long-range forces, the adsorbed film undergoes a first-order thin–thick transition from being molecularly thin to being substantially thicker. At higher temperatures the long-range forces gradually change to favor wetting. Thus, the film thickens

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continuously and a critical wetting transition occurs. This is the situation for the pentane on water and for the hexane on brine systems.⁸

On the other hand if the long-range forces favor wetting at lower temperatures than the short-range, the adsorbed film remains molecularly thin up to the point at which the short-range forces first favor wetting. The film then jumps discontinuously in thickness to being indefinitely thick, behavior known as a first-order wetting transition.

Notice that, in both cases, at some temperature there is a first-order transition between films of different thickness. These transitions persist if the pressure of the alkane vapor is reduced to slightly below its saturated value, so that a line of thin–thick transitions extends into the one-phase region of the bulk phase diagram. For systems showing first-order wetting, these transitions are known as “prewetting”⁹ and have been seen in a methanol–cyclohexane system¹⁰ for example.

In this paper our attention is not with these surface phase transitions as such but rather with the properties of “line” and “boundary” tensions in *n*-alkane–water systems.¹¹ For partial wetting, we consider the line tension associated with the three-phase contact line at the edge of alkane droplets sitting at the water surface. This is a quantity that has been measured by several groups recently.^{12,13} For both the thin–thick transitions seen in the critical wetting systems and the prewetting transitions seen in first-order wetting systems, we consider the boundary tension of the one-dimensional interface between the two coexisting surface phases. While no experimental measurement of this quantity has been reported, it is important in determining the lifetime of wetting films,¹⁴ and we include it in our discussion for completeness.

Our purpose is not to make quantitative calculations which can be compared with experimental results for a particular system, although we hope that our results are more than qualitatively reliable, but rather we aim to highlight interesting behavior that might be observed. To this end, although we choose some physical parameters that are specific to a particular *n*-alkane (pentane), others are extended beyond those values that are strictly valid for this system but not to the extent that they become unreasonable. As an example, we consider temperatures from 53 to about -70 °C, extending the variation of the Hamaker constant continuously through 0 °C, even though in reality there would be a discontinuity when the water freezes.

The method we use for these calculations is outlined in section 2. Since the various stages are already well documented,^{6,15,16} our discussion concentrates on the “data set” of physical parameters required as input. Sections 3 and 4 present our numerical results. We end in section 5, giving a quick comparison with some recent experimental measurements.

2. Theory

Our method of calculating the line and boundary tensions separates into two parts. The first is the calculation of an interface potential for the adsorption of a liquid alkane layer, details of which may be found in ref 15. In the second part, the tensions

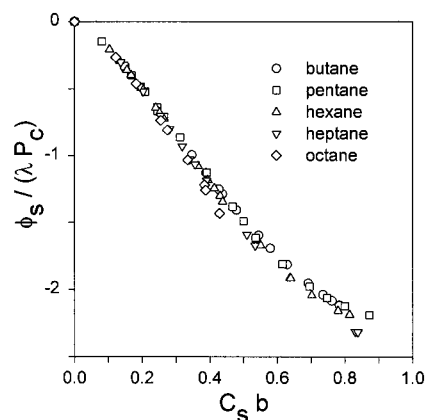


Figure 1. Universal dependence of the reduced surface free energy $\phi_s/(\lambda P_c)$ on the scaled surface concentration $C_s b$ for various *n*-alkanes at 15 °C. Values are calculated from the surface pressure measurements of refs 18 (butane) and 19 (pentane through octane).

are calculated directly from the interface potential using simple integral formulas from ref 16.

2.1. Interface Potential. We outline a recent generalization of the Cahn theory of wetting⁹ to include the thermodynamic properties of alkanes⁶ and long-range forces.¹⁵ This starts with an expression for the free energy of the water–alkane vapor interface γ relative to that of a water–pure water vapor interface

$$\gamma[C] - \gamma_0 = \int_0^\infty \left[\Delta f(C, C_0) + \frac{m}{2} \left(\frac{dC}{dZ} \right)^2 \right] dZ + \phi_s(C_s) - \int_\zeta^\infty H(Z)C(Z) dZ \quad (1)$$

The surface of the water phase, lying below the (*xy*) plane, is sharp so that the alkane density $C(Z)$ vanishes for $Z < 0$. At large distances from the water surface $Z \rightarrow \infty$, the alkane density tends to the value in the vapor C_0 .

The first term in the first integrand in (1) is the free energy density of a uniform fluid with density $C(Z)$ in excess of the free energy density of the bulk gas phase. Following ref 6, we use a form derived from a “Peng Robinson” equation of state¹⁷

$$P = \frac{CRT}{1 - Cb} - \frac{a(T)C^2}{1 + Cb(2 - Cb)} \quad (2)$$

where P is the pressure, R is the gas constant, and T is the temperature. The molecular interaction term at the critical temperature $a(T_c)$ and the excluded volume b can be deduced from the critical temperature T_c and pressure P_c . An additional acentric factor w determines the temperature variation of a .¹⁷

The second term in (1) involves the “influence parameter” m . This may be determined from measurements of the interface tension between the two bulk alkane phases, although we use a handy semiempirical formula given in ref 6. A convenient length scale can now be introduced, $\lambda = (m/b^2 P_c)^{1/2}$, which typically takes a value of about 35 Å for the *n*-alkanes considered. Natural units of surface and line tensions can be defined by multiplying the critical pressure P_c by appropriate factors of λ .

The next term in (1), ϕ_s , represents short-range forces at the water surface as a contact interaction that depends only on the alkane density at the surface $C_s = C(Z=0)$. In ref 6 this interaction was deduced from the measured dependence of the water–alkane surface pressure on the alkane vapor pressure at 15 °C.^{18,19} In principle it is a different function for each of the *n*-alkanes, but as shown in Figure 1 we find that by scaling ϕ_s with the unit of surface tension λP_c and the density with the excluded volume b ,

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a remarkable collapse of the data from butane to octane occurs. We do not claim that our choice of reduced variables gives the best possible collapse, but it seems reasonable given that $c_s = C_s$ b is proportional to the surface density of carbonyl units.

Although a good fit to the experimental data for ϕ_s can be made with a fourth-order polynomial,⁶ it suffices for our purposes to adopt a simpler two-term expansion which is faithful to the data for densities close to the liquid-phase density

$$\frac{\phi_s(c_s)}{\lambda P_c} = \text{const} - h_1 c_s - \frac{g}{2} c_s^2 \quad (3)$$

taking h_1 and g to be 5.45 and -5.58 , respectively. Surface pressure data at temperatures between 11 and 50 °C for butane¹⁸ indicate that the temperature variation of h_1 and g can be neglected.

The final term in (1) represents the long-range component of the intermolecular forces and is assumed to have a power-law dependence on Z , $H(Z) = H_3/Z^3 + H_4/Z^4$. The leading coefficient is related to the Hamaker constant for the system $W = -6\pi H_3 (C_L - C_G)$, where C_L and C_G are the densities of the coexisting alkane liquid and gas phases. For pentane this has been calculated between 15 and 70 °C using an approximate method,⁵ and more elaborate calculations based on DLP theory confirm the accuracy of these results at 20 °C.²⁰ The variation with temperature is almost linear with $W = W_T(T_0 - T)$, where W_T is of the order $5.5 \times 10^{-23} \text{ J K}^{-1}$. Following ref 15 we incorporate this into our calculations by assuming a linear temperature variation for the reduced variable $a_3 = H_3 C_L / (P_c \lambda^3) = u(T - T_0)/T_0$, where the coefficient $u = 0.0147$. Because pentane undergoes a critical wetting transition on water, T_0 is identified with the wetting temperature 53 °C. In our calculations, we study the effect of varying T_0 . To some extent, this mimics the effect of adding salt to the water, which reduces T_0 but leaves the value of W_T almost unchanged.²¹

The second term H_4 in the expansion of $H(Z)$ can also be estimated close to a continuous wetting transition, where the adsorbed layer thickness l is approximately given by $l \approx H_4/|H_3| \sim (T_0 - T)^{-1}$. For pentane the divergence of l has been measured by ellipsometry,⁵ so that a value for H_4 close to T_0 can be deduced. Again, we use a reduced variable $a_4 = H_4 C_L / (P_c \lambda^4) = 1.112 \times 10^{-3}$ and ignore any temperature variation in this parameter. In fact, as we show below, the line tension close to a critical wetting transition is independent of the value of H_4 . For first-order wetting and for thin-thick transitions, we also find that the line and boundary tensions are not especially sensitive.

Finally, we need to specify a short distance cutoff ζ in the final term of (1). This is not a quantity that can be measured and must be chosen so that its value is physically reasonable (of the order of a molecular diameter). We also choose that it is sufficiently large that it does not influence the results for the film thickness or the free energy when the surface is covered by a thin alkane film. Following ref 15 we take $\zeta/\lambda = 0.2$, corresponding to about the size of an n -alkane molecule.

Our method of including long-range forces via the term $H(Z)$ must be viewed as an approximation. From the form of (1) it would appear that only interactions between the spectator phase (water) and the alkane are taken into account, whereas the Hamaker constant used to determine H_3 includes interactions between alkane molecules. However we believe that provided the long-range tails of the van der Waals interactions are sufficiently weak, we are making a valid approximation. When this condition is not met, a simple local functional like (1) is no longer valid and significantly more complicated density functional theories are required.²

When each of the terms in (1) are known, the free energy functional can be minimized with respect to variations of $C(Z)$ to yield the equilibrium density profile of the alkane film. In addition, it can be minimized with a constraint that the alkane forms a layer of nominal thickness l , defined so that $C(Z = l)$ takes a value C_X intermediate between that of the liquid and gas phases. For reasonable values, the dependence of our results on

C_X is not significant. Following ref 15, we choose $C_X = C_G + 0.1(C_L - C_G)$. The minimized free energy can then be written as a simple function of the constrained layer thickness l

$$\gamma(l) = \min(\gamma[C]) + V(l) \quad (4)$$

For cases of partial wetting, the interface potential $V(l)$ has an absolute minimum at finite thickness l_1 such that $V(l_1) = 0$. The limiting value for large l , $E = \lim_{l \rightarrow \infty} V(l)$ is related to the contact angle θ by $E = \gamma_a(1 - \cos \theta)$, where γ_a is the surface tension of the alkane and is the inverse of the "spreading coefficient" $S = -E$. The nature of the wetting transition is determined by the behavior of this minimum as the temperature is raised. If the equilibrium thickness l_1 slowly increases with temperature, the system undergoes a continuous wetting transition as $l_1 \rightarrow \infty$. On the other hand, if the minimum jumps discontinuously from a finite value of l to a value approaching infinity, then there is a first-order wetting transition. Similarly, thin-thick transitions of the type discussed in the Introduction occur when the absolute minimum of $V(l)$ switches between two local minima l_1 and l_2 .

2.2. Line and Boundary Tensions. The interface potential $V(l)$ represents the free energy per unit area of a uniform alkane film of thickness l . We now consider films that vary in thickness over the water surface, so that l is a function of position in the (xy) plane. For simplicity we consider films that vary in the x direction only, although that does not restrict the applicability of our results. A common approximation is to write the free energy as a simple local functional of the thickness $l(x)$ ¹⁶

$$\Omega[l] = \int \left[\frac{\gamma_a}{2} \left(\frac{dl}{dx} \right)^2 + V(l) \right] dx \quad (5)$$

where γ_a is the tension of the (free) alkane liquid-vapor interface. By minimizing this free energy with respect to variations in the film thickness and solving the resulting Euler-Lagrange equation with appropriate boundary conditions, one can derive a simple integral formula for the line tension τ of a droplet¹⁶

$$\tau = (2\gamma_a)^{1/2} \int_{l_1}^{\infty} [V(l)^{1/2} - E^{1/2}] dl \quad (6)$$

where l_1 is the thickness of the partial wetting layer surrounding the droplet (that value of l which minimizes V). Similarly, the boundary tension for the interface between two coexisting surface phases of thickness l_1 and l_2 is¹⁶

$$\tau_b = (2\gamma_a)^{1/2} \int_{l_1}^{l_2} V(l)^{1/2} dl \quad (7)$$

where (by its definition) $V(l)$ vanishes at the two limits of integration.

Some comments about the *sign* of the line and boundary tensions are in order. From (7) it is clear that τ_b is never negative, as must be the case if the two surface phases separated by such a boundary are to be thermodynamically stable. However, eq 6 allows no general statement to be made about the sign of the line tension, other than at the wetting transition itself ($E = 0$), where τ cannot be negative. In fact approaching a critical wetting transition, the line tension tends to the value zero, whereas at a first-order wetting transition, the line tension has a nonzero, positive limit.¹⁶ In both cases, the approach to the value at wetting is from below.

In the vicinity of a critical wetting transition, the thickness of the wetting film l_1 becomes very large. Unfortunately this makes it numerically very difficult to calculate the density profile $C(Z)$ and the interface potential $V(l)$, and a numerical calculation with quadruple precision is needed.¹⁵ However in these cases, it is sufficient to adopt a simple (truncated) expansion form for the interface potential involving the Hamaker constant W and a next-to-leading term B

$$V(l) = -\frac{W}{12\pi l^2} + \frac{B}{l^3} + E \quad (8)$$

where E is chosen so that $\min(V(l)) = 0$. Substituting this simple

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form for $V(l)$ into (6), we find for the line tension

$$\tau = -\frac{1}{3}2^{-1/6} \left(\frac{\gamma_a W}{\pi} \right)^{1/2} M(3) \quad (9)$$

where $M(3) \approx 0.949$ is a definite integral given in ref 16. Notice that, by happy coincidence, this result depends only on the alkane surface tension γ_a and the Hamaker constant W but not on the coefficient B .

Finally we must remark that the validity of the local functional (5) for fluids with long-range interactions has been questioned recently, and it has been suggested that the results of this kind of approach differ significantly from those of more microscopic, density functional theories.²³ However, it has now been established that the reported differences arose from numerical problems with the minimization procedure used in ref 23, and in fact the local functional approach is quantitatively valid.²⁴

3. Short-Range Forces

We begin our presentation of numerical results by considering the wetting behavior of the *n*-alkanes when long-range forces are not included in our calculation, ignoring the final term in (1). In later sections we reintroduce these forces for pentane, the case for which they are known with the most precision. By studying the manner in which the results are effected for that case, we are able to draw conclusions about the applicability to the remaining *n*-alkanes of the results in this section.

Because the bulk free energy term Δf and the surface free energy ϕ_s in (1) are similar for each of the *n*-alkanes when expressed in units of the critical temperature and pressure (the only difference arises from the different values of the small parameter w in the temperature variation of $a(T)$), the wetting behavior predicted by the short-range theory is also very similar. A first-order wetting transition is found at a temperature T_{sr} that expressed in terms of the bulk critical temperature T_{sr}/T_c varies approximately linearly with chain length between 0.49 for butane and 0.56 for octane. This is equivalent to a range of temperatures from -65 to 48 °C. With the possible exception of butane, these temperatures cannot be identified with the wetting temperature for the fluid because they are significantly too low to be compatible with experimental observations of partial wetting.⁴ In some part, this is due to our omission of long-range forces, which disfavor wetting at these predicted wetting temperatures. However in the next section we show that such long-range forces do allow a thin–thick transition at a temperature close to T_{sr} . Thus for the case of pentane, the calculated transition temperature ($T_{sr} = -29$ °C) is not in contradiction with the observed thick film at room temperature, although there is a problem with the thin film at room temperature for the case of hexane ($T_{sr} = -3$ °C). We conclude that the values predicted for the wetting temperatures with the short-range theory are not as close to the temperature of a possible thin–thick transition as one would like, and we are not able at present to explain the deviation.

The behavior of the line tension τ and boundary tension τ_b within the short-range theory for the case of pentane is shown in Figure 2. For the other *n*-alkanes, both the magnitude of the tensions and the temperature variation are very similar, so that the figure can be considered to apply equally to each.

The most notable features are the steep cusps in both τ and τ_b at the predicted wetting temperature T_{sr} , in

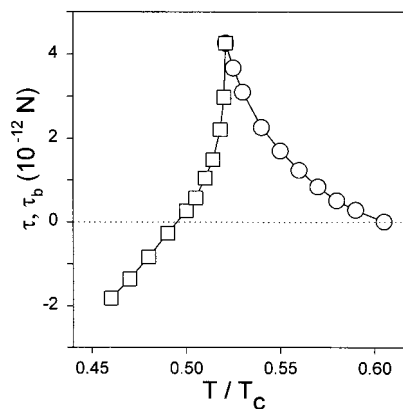


Figure 2. Line and boundary tension for pentane, from calculations taking only short-range forces into account. There is a first-order wetting transition at $T_{sr}/T_c = 0.52$. Square and circular data points represent calculated values for line and boundary tensions, respectively. Both tensions reach a common finite value at T_{sr} .

accordance with the general expectation for systems with short-range forces.^{11,25} Both tensions attain a common, maximal and positive value of about 4×10^{-12} N. At temperatures below the wetting transition the line tension is positive only within a narrow window corresponding to about 10 °C, over which the contact angle changes from 0° to about 15° . Further from the transition τ becomes gradually ever more negative, and we do not find any minimum value.

The line of prewetting transitions along which τ_b is defined extends from T_{sr} up to a prewetting critical point about 40 °C higher. The boundary tension diminishes continuously along this line and vanishes at the prewetting critical point.

4. Short- and Long-Range Forces

We now reintroduce the long-range forces ignored in the previous section for the specific case of pentane. In section 4.1 we consider the realistic situation, where the long-range forces prevent wetting up to a temperature above the short-range wetting temperature T_{sr} so that a critical wetting transition results. The opposite case, where the long-range forces first favor wetting below T_{sr} so that a first-order wetting transition occurs close to T_{sr} , is considered in section 4.2.

4.1. Critical Wetting. In accordance with calculations^{5,20} we include the effect of a Hamaker constant that vanishes at a temperature $T_0/T_c = 0.69$, equivalent to 53 °C. The wetting film now undergoes two transitions. At $T_{w1}/T_c = 0.51$, slightly below the short-range wetting temperature $T_{sr}/T_c = 0.52$ calculated for pentane in section 3, the film undergoes a thin–thick transition, where the film jumps from being molecularly thin (4 Å) to mesoscopically thick (30 Å). This occurs when the short-range forces first favor wetting, but the film is prevented from becoming indefinitely thick by the positive Hamaker constant. As the temperature increases, the Hamaker constant slowly decreases and the film thickens, becoming indefinitely thick at T_0 .¹⁵

The behavior of the line tension is shown in Figure 3. In the vicinity of T_{w1} , it is very similar to the line tension calculated with just short-range forces in Figure 2, increasing sharply on approach to the thin–thick transition and reaching a maximum value of approximately 5×10^{-12} N.

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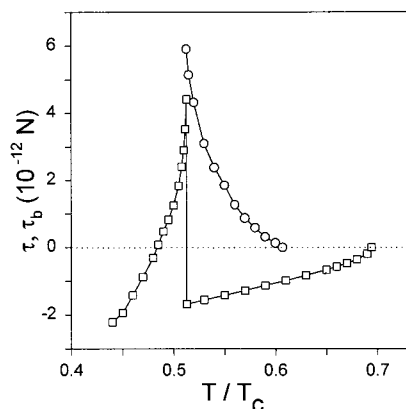


Figure 3. Line and boundary tension for pentane, from calculations including long-range forces for which the Hamaker constant vanishes at $T_0/T_c = 0.69$. A thin–thick transition occurs at $T_w/T_c = 0.51$, and a critical wetting transition at T_0/T_c . Calculated values of the line tension are represented by squares. A line of thin–thick transitions also extends upward from T_w , and calculated values for the boundary tension along this line are shown as circles. At T_w , the jump in line tension is equal to the boundary tension between thin and thick surface phases.

Above this transition the surface is still partially wet, so that droplets exhibit a nonvanishing contact angle and the line tension is still defined. However, the structure of the contact line changes radically. Whereas below the transition, the contact line is a region where a thin film meets the edge of liquid droplets, above the transition droplets sit atop a mesoscopic film. At the transition itself, the contact line splits into a boundary line between the thin and the mesoscopic film and a contact line where the mesoscopic film touches the edge of the liquid droplet (such a situation is discussed in section 6.2 of ref 26 and references therein).

This sudden change in structure is reflected in a discontinuity of the line tension. As the maximum is reached approaching the thin–thick transition from below, the line tension becomes equal to the sum of a boundary tension between the thin and thick regions and a line tension between the thick film and droplet. This is akin to Antonow's rule for surface tensions²⁷ and a similar rule for line tensions.²⁸ Above the thin–thick transition, only the thick film survives so that the line tension suddenly drops by an amount equal to the boundary tension of the thin–thick boundary, about 7×10^{-12} N.

In fact at the thin–thick transition, a small systematic error enters into our calculation. By inspection of eqs 6 and 7, it can be seen that there is a difference between the sum of the thin–thick boundary and thick film line tensions and the thin film line tension. This difference is equal to $(2\gamma_a)^{1/2} E^{1/2} \Delta l = \gamma_a (\sin \theta) \Delta l$, where Δl is the difference in film thickness and θ is the contact angle. This is inherent in our interface potential approach, which assumes that the third coexisting phase (water) constitutes a rigid substrate for the adsorbed alkane. As a result, an unbalanced vertical force $\gamma_a \sin \theta$ acts at the contact line and introduces a dependence of the line tension on the particular choice (made explicit in ref 16) of dividing surfaces for the three coexisting phases.²⁷ For the usual case of a droplet coexisting with a single partial wetting film, the horizontal dividing surface is predetermined during the derivation of the interface potential to be

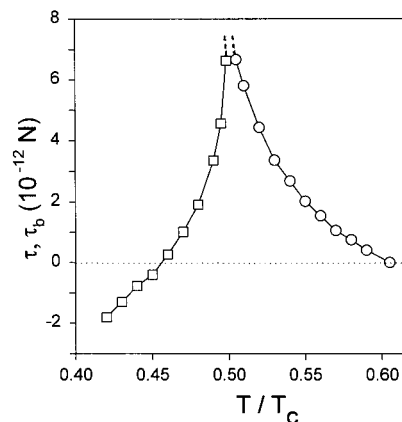


Figure 4. Line and boundary tensions for pentane, from calculations including long-range forces for which the Hamaker constant first vanishes at $T_0/T_c = 0.35$. A first-order wetting transition occurs at $T_w/T_c = 0.50$. Square and circular data points represent calculated values for line and boundary tensions, respectively. Both tensions diverge at T_w .

coincident with the film. At a thin–thick transition, this choice of dividing surface becomes ambiguous. However for the case in hand, the discrepancy is equal to 0.7×10^{-12} N and is not particularly serious.

For temperatures above the thin–thick transition, the line tension is negative and rather smaller in magnitude. It diminishes continuously approaching the (critical) wetting transition at T_0 , according to (9), so that asymptotically $\tau \propto -(T_0 - T)^{1/2}$.

Also shown in Figure 3 is the boundary tension along the line of thin–thick transitions extending into the bulk one–phase region, discussed in section 1. This begins at T_w and extends up to a critical point about 40 °C higher. The boundary tension has a maximum value at T_w of about 6×10^{-12} N and reduces continuously to zero at the thin–thick critical point.

4.2. First-Order Wetting. Now we consider the effect of lowering the temperature for which $W = 0$ and $T_0/T_c = 0.35$, so that the Hamaker constant becomes negative before the short-range forces favor wetting. The system then remains partially wet until a first-order wetting transition occurs at a temperature $T_w/T_c = 0.50$, close to the short-range wetting temperature T_{sr} . The behavior of the line tension approaching this transition is shown in Figure 4, and in many respects it is similar to the behavior approaching the first-order wetting transition in Figure 2 and the thin–thick transition in Figure 3. However, the value of the line tension does increase more rapidly in the close vicinity of the wetting temperature and in fact diverges at the wetting transition in the manner $\tau \propto -\log(T_w - T)$.¹⁶

Above the wetting temperature, a prewetting line of thin–thick transitions persists, and the values of the boundary tension along this line are also shown in Figure 4. Like the line tension it diverges at the wetting transition and vanishes 40 °C above T_w at the prewetting critical point.

5. Conclusions and Outlook

In this paper we have shown that it is possible to make estimates of the line tension for *n*-alkanes spreading on water, using the Cahn-type theory developed previously for these systems.^{6,15} As far as we know, this is the first time that the line tension for a specific, real system has been calculated. Also, in re-analyzing the available data for the adsorption isotherms of a series of *n*-alkanes,^{18,19} we have found a remarkable universal curve for the

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interaction of the hydrocarbon chains at the water interface ϕ_s , which has potentially important applications for the prediction of the interfacial tension of water in the presence of alkane vapors.

In terms of the parameters that are required for the calculation of the line tension, our approach faces no major difficulties and could be applied to other systems for which both the bulk thermodynamic parameters and sufficient surface pressure data are available. While calculation of the long-range forces, and in particular the Hamaker constant, is a subtle matter which is all important for determining the wetting behavior, comparison of Figure 2 with Figures 3 and 4 shows that, under most conditions, the long-range forces do not significantly alter the magnitude of the line tension except either in the very close vicinity of a first-order wetting transition or approaching critical wetting. For most circumstances, the contribution to the line tension from the short-range forces is dominant.

Concerning the reliability of our results, let us now remark that the typical magnitude 10^{-12} N is smaller than that measured in some recent experiments. Dussaud and Vignes-Adler¹² reported values for *n*-octane on brine of between 9×10^{-11} and 1×10^{-9} N, whereas Aveyard et al. find a line tension 1.6×10^{-11} N for an *n*-decane/dodecanol mixture on water. For the first of these, the

discrepancy with our results is rather serious. It seems unlikely that the surface free energy ϕ_s for brine is sufficiently different from that on water to account for this, since the surface pressure is nearly independent of salt concentration.²⁹ The agreement with the result of Aveyard et al. is somewhat better, being about a factor 3 higher than we would expect for octane. The difference might be accounted for by the presence of small amounts of dodecanol, which would effect ϕ_s if it were adsorbed preferentially at the water-alkane interface.

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