Transition temperatures and contact angles in the sequential-wetting scenario of \( n \)-alkanes on (salt) water

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Abstract

Alkanes of medium chain length show an unusual wetting behavior on (salt) water, exhibiting a sequence of two changes in the wetting state. When deposited on the water surface at low temperatures, the liquid alkane forms discrete droplets that are interconnected only by a molecularly thin film. On increase of the temperature, there occurs a sudden jump of the film thickness and, at this first-order transition, a mesoscopically thick layer of liquid alkane is formed. Heating the system further leads to a divergence of the film thickness in a continuous manner. While the long-range forces between substrate and adsorbate are responsible for the critical transition, which occurs at the temperature at which the Hamaker constant changes sign, it is primarily the short-range components of the forces that bring about the first-order transition. We calculate the Hamaker constant of the system and show how, within a modified Cahn theory, accurate predictions of the first-order transition temperatures can be obtained for \( n \)-alkanes (pentane and hexane) on water and even on brine. Furthermore, we study the variation of the contact angle as a function of temperature.

Keywords: Wetting; Interfacial tension; Electrolytes; Method of calculation

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1. Introduction

In recent experiments, \( n \)-alkanes of medium chain length (pentane, hexane, and heptane) have been observed to undergo two, instead of just one, changes of the wetting state when they are deposited on (salt) water and the temperature is raised subsequently \([1,2,3]\). At sufficiently low temperature, the deposited liquid alkane, which is at coexistence with its vapor, forms discrete droplets on the surface of the substrate. These droplets make a non-zero contact angle with the substrate surface and, for volatile substances like alkanes of relatively low molecular weight, are interconnected only by a molecularly thin film. This state is referred to as partial wetting.

At high enough temperatures, on the other hand, there will be a macroscopically (in principle, infinitely) thick film of liquid alkane covering the (salt) water surface completely. The contact angle in this so-called complete-wetting state is exactly zero. The transition between these two states can, in general, occur in two qualitatively different fashions: at a first-order transition, one observes an abrupt change of the film thickness from microscopic to macroscopic values; likewise, the contact angle \( \theta \), which becomes smaller with increasing temperature, vanishes and, in doing so, its derivative with respect to temperature displays a square-root singularity of the form \( d\theta/dT \sim (T_w - T)^{-1/2} \), where \( T_w \) denotes the wetting-transition temperature. In the second and much rarer case, the film thickness diverges continuously on approach of the wetting temperature \([4,5]\). This type of wetting transition is, therefore, referred to as being continuous or ‘critical’. Although predicted earlier from theoretical considerations \([6,7]\), it had escaped experimental observation until recently. For an \( n \)-nonane/methanol mixture, for which the wetting transition temperature is very close to the consolute point, so that bulk fluctuations become important, a logarithmic divergence of the film thickness on approaching \( T_w \) has been observed \([5]\), as well as a vanishing of the contact angle according to the power law \( 1 - \cos \theta \sim (T_w - T)^{2-\alpha_s} \), with \( \alpha_s \) being the surface specific heat exponent and having a numerical value of \( -0.2 \pm 0.3 \), which is compatible with short-range critical wetting \( (\alpha_s = 0, \text{ implying } \theta \sim (T_w - T)) \), but not with first-order wetting \( (\alpha_s = 1) \). In the case of long-range critical wetting, in contrast, which was observed first for pentane on water, one finds a power-law divergence of the film thickness of the form \( l \sim (T_w - T)^{-1} \) \([4]\) (and the contact angle vanishes according to \( \theta \sim (T_w - T)^{3/2} \), corresponding to a surface specific heat exponent of \( \alpha_s = -1 \)). This behavior follows from the leading terms of the tails of the long-range forces between substrate and adsorbate \([7]\).

By now, it has become apparent that such a long-range critical wetting transition is a generic feature of all \( n \)-alkanes of medium chain length on water or brine, respectively \([2,3,8]\). Salt was originally added to the aqueous substrate to decrease the wetting temperature in such a way that the transition occurs in the experimentally accessible range of \( 0 - 80 \degree C \), i.e. for experimental convenience \([1]\), but the cases in which brine, rather than pure water, is the substrate seem to be more relevant in industrial and environmental situations of practical interest, for example in secondary oil recovery \([3,9,10]\).

The occurrence of long-range critical wetting in systems of alkane on (salt) water gives rise to another peculiar feature: the transition from partial to complete wetting
takes place in two steps instead of just one! [1] As mentioned above, the true wetting transition to complete wetting is continuous and brought about by long-range forces between substrate and adsorbate, which change their nature from inhibiting complete wetting to supporting it at this temperature, \( T_{w,c} \). This critical transition, however, is preceded by a first-order transition at a lower temperature, \( T_{w,1} \), at which the film thickness shows an abrupt increase from being molecularly thin to a mesoscopic value (6–15 nm) [1,2]. Accordingly, the temperature-derivative of the contact angle shows a finite discontinuity (while \( \theta \) itself is a continuous function of \( T \)) at \( T_{w,1} \), which would be (very close to) the first-order wetting transition temperature if the long-range forces did not oppose complete wetting, i.e. the formation of a macroscopic wetting layer, at this lower temperature. The occurrence of such a transition, the first-order nature of which is corroborated by the experimentally observed hysteresis in the film thickness [1], is attributable to the short-range parts of the forces, as taken into account in Cahn’s original theory of wetting transitions [4,12,13].

For the intermediate state, in which a film of mesoscopic thickness is present, the term ‘frustrated-complete wetting’ has been coined [9]. For a typical film thickness of 100 Å, the contact angle of the droplets that sit on top of this layer is very small (<1°), indicating that this state is energetically very close to complete wetting [2,11]. In this state, the efficiency of oil recovery by drainage from a model reservoir is also similar to that from a system in the complete wetting state [3]. On grounds of dynamic arguments, however, one expects considerable differences to the flow in a system with a truly macroscopic wetting layer [14]. Therefore, accurate knowledge of both transition temperatures is highly desirable.

In the next section, we will outline the main features of a complete and consistent mean-field theory of the wetting behavior of \( n \)-alkanes of medium chain length (pentane and hexane) on pure water and on brine, respectively, for various concentrations of salt. In section 3, we will compare the results of our theory to experimental findings and predict the transition temperatures and contact angles for systems for which these properties have not been measured yet. Section 4 concludes the paper, assesses the current state of the theory and experiments on the sequential wetting of \( n \)-alkanes on aqueous substrates and briefly outlines plans for future investigations.

2. Methodology

The wetting state, in which a system consisting of three phases (the substrate (s), which may be solid or liquid, the liquid (l) phase of the adsorbate and vapor (v)) is present, is determined by the interfacial tensions between the three pairs of them, which we denote by \( \gamma_{sl}, \gamma_{sv} \) and \( \gamma_{lv} \). According to Young’s law, the contact angle is given by \( \gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos \theta \). In the partial-wetting state, \( \gamma_{sv} < \gamma_{sl} + \gamma_{lv} \) and, therefore, \( \theta > 0 \), while for complete wetting, the \( sv \)-interface is replaced an \( sl \)-interface and an \( lv \)-interface and, accordingly, Antonow’s rule \( \gamma_{sv} = \gamma_{sl} + \gamma_{lv} \) holds. The contact angle is then zero. In the special case of sequential wetting, the ultimate transition to complete wetting, which occurs at \( T_{w,c} \), is determined by the location at which the Hamaker constant changes sign, i.e. where the leading term of the algebraic tails of the long-range forces starts to favor having a thick wetting layer on top of
the substrate, instead of opposing the formation of such a layer, which keeps the system in the frustrated complete wetting state for $T_{w,1} \leq T \leq T_{w,c}$. The first-order transition between a thin and a mesoscopically thick film, however, is not a true wetting transition. Its location is determined mainly by short-range forces [12, 15], but the long-range tails, which are treated perturbatively in our approach, make a quantitative difference [16]. $T_{w,1}$ is found by comparing the interfacial free energies of the situations corresponding to having only a molecularly thin film present in the density profile of an $sv$-interface and to having a mesoscopically thick film – only one of these two will be stable, the other just metastable, except for right at $T_{w,1}$, where both are equal in free energy per unit area (coexistence of thin and thick film).

To calculate the interfacial tensions, we employ a modified Cahn theory augmented for algebraically decaying long-range forces, which are treated in a perturbative fashion. The free-energy functional, which is to be minimized with respect to the density profile of the adsorbate, $\rho(z)$, reads [16]:

$$\gamma[\rho] = \gamma_0 + \phi(\rho_0) + \int_{\Delta z}^{\infty} \left\{ \Delta f(\rho, \rho_{bulk}) + \frac{c}{2} \left( \frac{d\rho}{dz} \right)^2 \right\} dz$$

$$+ \left\{ \Delta f(\rho_0, \rho_{bulk}) + \frac{c}{2} \left[ (\rho_0 - \rho_1) / \Delta z \right]^2 \right\} \Delta z$$

$$- \int_{\Delta z}^{\infty} \left( \frac{a_3}{z^3} + \frac{a_4}{z^4} \right) \rho(z) dz - \int_{\Delta z}^{\infty} \left( \frac{a_3'}{(z + \delta)^3} + \frac{a_4'}{(z + \delta)^4} \right) \rho(z) dz$$

$$- \frac{a_3'}{\delta^3} \rho_0 \Delta z. \quad (1)$$

The first three terms are the ingredients of standard Cahn theory (with $\Delta z = 0$) [13]: the first one describes the surface tension of the substrate against vacuum; it is irrelevant to the wetting properties and no value for it needs to be specified. In the second term, $\phi$ denotes the so-called contact energy, which describes the short-range interaction between the substrate and the adsorbate; therefore, it only depends on the density of the adsorbate right at the substrate surface, $\rho(0) = \rho_0$. The $z$-axis is chosen perpendicular to the substrate surface and only the half space $z \geq 0$, in which the adsorbate is present, is considered explicitly. $\phi(\rho_0)$ is usually represented in a quadratic form: $\phi(\rho_0) = -h_1 \rho_0 - g \rho_0^2 / 2$; the coefficients $h_1$ and $g$ can be deduced from measurements of the surface pressure [15, 17]. The third term concerns the cohesive properties of the adsorbate, like in the classical theory of the liquid–vapor interfacial tension of van der Waals [18]: $\Delta f(\rho, \rho_{bulk})$, to be calculated from the Peng–Robinson equation of state in this case, measures the excess free energy of locally having a density $\rho(z)$ over having either of the bulk densities $\rho_{bulk}$; the second term in the integral is the square-gradient term, which penalizes inhomogeneities of the density. The coefficient $c$ is the influence parameter and is obtained by matching the computed liquid–vapor interfacial tensions to experimental results [19]. In the modified Cahn theory, these two terms are to be integrated over from $\Delta z$ to infinity, instead of integrating from zero to infinity as in standard Cahn theory [13]. The first layer of adsorbed alkane molecules, which is of molecular thickness ($\Delta z = \sigma$, the diameter of an adsorbate molecule) is treated in a lattice-gas approach, ensuring that states
of low adsorption are properly accounted for \cite{15}. This discretized version of Cahn theory yields the next term in Eq. \ref{eq:1} – its ingredients are otherwise the same as in the continuum version. For brevity, the density at a distance of one molecular diameter from the substrate surface is denoted by $\rho_1 = \rho(\Delta z)$.

The last three terms on the right-hand side of Eq. \ref{eq:1} incorporate the long-range interaction into the free-energy functional. The underlying picture of the system in the computation of the long-range contribution is a five-layer structure \cite{16}: even if the substrate is brine, there is a thin layer of pure water (the so-called depletion layer) at the brine/alkane interface \cite{20,21}, so that it is always pure water that is in direct contact with the adsorbed alkane. A third (conceptual) medium is formed by the dense liquid layer of adsorbed alkane molecules which are in direct contact with the aqueous substrate \cite{3,22}. Moving away from the substrate surface, this layer is followed by the bulk liquid alkane and, ultimately, by the vapor phase. While the brine and the vapor phases are semi-infinite, the pure-water layer is of thickness $\delta$ (to be identified with the hydration radius of an ion \cite{21}), the first layer of adsorbed dense liquid alkane has a spatial extent of one molecular diameter $\sigma = \Delta z$, and the film thickness of liquid alkane is denoted by $l$.

For pure water as the substrate, the last two terms in Eq. \ref{eq:1} vanish. The first of the three terms of the long-range field describes the interaction between the water layer and the adsorbate; the cutoff $z_c$ is numerically very close to $1.5\sigma$, the distance of closest approach of adsorbate particles that are not part of the first layer. The second integral concerns the long-range interactions between brine and the adsorbate across the intervening water layer of thickness $\delta$, which is reflected by having $(z + \delta)$ instead of just $z$ in the denominators of the first couple of leading terms taken into account here. The last term in Eq. \ref{eq:1} contains the remaining contribution which arises from the interaction of brine with the first layer of adsorbed alkane molecules – this interaction is not included in the preceding term since $z_c > \sigma$.

The amplitudes of the tails of the long-range field, $a_3$, $a_4$, $a'_3$ and $a'_4$ are calculated from a five-layer Dzyaloshinskii–Lifshitz–Pitaevskii theory that invokes Israelachvili’s simplifications to the dielectric spectrum \cite{23}, which allows one to obtain the long-range field from the static dielectric permittivities, $\varepsilon_j(0)$, the indices of refraction, $n_j$, and a common characteristic UV absorption frequency of the different media. The explicit formulas for the amplitudes can be found in the more detailed article \cite{16}.

The current theory offers a complete and consistent description of the wetting behavior of $n$-alkanes on water or brine, as we will show in the next section.

\section{Results and discussion}

We employ the theory outlined in the preceding section to calculate the transition temperatures as a function of the salinity of the substrate and contact angles as a function of temperature in the sequential wetting of $n$-alkanes, namely pentane and hexane, on salt water. Figure 1 shows the calculated first-order and critical transition temperatures for pentane and hexane, respectively, on brine in the concentration range $0 \leq c_{NaCl} \leq 2.5 \text{ mol/L}$. The experimental points for the respective transition temperatures for hexane on brine \cite{1} and for pentane on water \cite{10,2} are indicated
by open symbols. The overall agreement is very good, indicating that the theory incorporates the most important effects that lead to sequential wetting even quantitatively. Note that the first-order transition temperatures for pentane on brine are below the freezing point of the substrate for \( c_{\text{NaCl}} > 2.1 \text{ mol/L} \). Furthermore, it is seen that, within the theory, the line of first-order transition temperatures is almost parallel to the line of critical-transition temperatures for pentane on brine, too, just as it was observed experimentally for hexane on brine \([1]\). An experimental check of this prediction is desirable.

To test the validity of the more or less arbitrary division of the forces acting between substrate and adsorbate into short-range and long-range parts, and of the perturbative treatment of the long-range parts, it might be useful to take a closer look at the contact angles, in particular in the frustrated-complete wetting state. In this latter state, the contact angle is very small (\(<1^\circ\) ), indicating that the relatively large film thickness of \( l \geq 60 \text{ Å} \) is sufficient to decouple the two interfaces (\( sl \) and \( lv \)) almost completely \([11]\). In the context of the present theory, the contact angle can, asymptotically, be evaluated from the long-range part alone \([3]\). To accomplish this, one uses the fact that the contact angle is related to the spreading coefficient through \( S = \gamma_{lv}(\cos \theta - 1) \). We consider the free-energy difference between the \( sv \)-interfaces in the complete wetting (\( cw \)) state and the frustrated-complete wetting (\( fcw \)) state, the origin of which lies completely in the range of distances between \( l \) and infinity from the substrate. Using \( S_{cw} = 0 \) and the fact that \( \rho(z) \) is practically equal to \( \rho_l \) for \( cw \), while it is almost zero (the vapor phase is very dilute) in this range for \( fcw \),
Fig. 2: Contact angles of pentane on pure water (thin line) and of hexane on brine for $c_{NaCl} = 2.5$ mol/L (thick line) as a function of temperature. The transition temperatures are $T_{w,1} = 294.5$ K and $T_{w,c} = 316.7$ K for hexane on brine and $T_{w,1} = 298$ K and $T_{w,c} = 325.4$ K for pentane on water. A value of 1.77 Å has been used for $\delta$ in these cases.

We obtain for the spreading coefficient in the $fcw$ state:

$$S_{fcw} = \rho_l \int_{l}^{\infty} \left( \frac{a_{3}}{z^{3}} + \frac{a_{4}}{z^{4}} \right) dz.$$  \hspace{1cm} (2)

Noting that, asymptotically for large $l$, the film thickness will be given by $l \approx -a_{4}/a_{3}$, we arrive at

$$1 - \cos \theta = -\frac{\rho_{l}}{6 \gamma_{lv}} \frac{a_{3}}{a_{4}}.$$  \hspace{1cm} (3)

For partial wetting, we obtain $\theta$ from Young’s law, explicitly calculating $\gamma_{sv}$, $\gamma_{sl}$ and $\gamma_{lv}$ by numerical minimization, which causes the somewhat noisy results for the contact angle in this wetting state. Figure 2 shows $\theta$ as a function of temperature for pentane on pure water and for hexane on brine ($c_{NaCl} = 2.5$ mol/L) \[24\]. It is seen that not only the transition temperatures for these two systems are very similar, but also the contact angles. The discontinuity of $d\theta/dT$ is clearly visible at $T_{w,1}$.

In Fig. 3, we focus on the behavior of the contact angle in the frustrated-complete wetting state; in this state, our data obtained from direct numerical minimization are too noisy and, therefore, useless because the energetical differences between the $cw$ and $fcw$ states are very small. The figure shows the analytical results obtained from relation (3), which is asymptotically valid in the case $l \rightarrow \infty$. From this equation, it can also be read off that $\theta$ is expected to vanish as $\theta \sim (T_{w,c} - T)^{3/2}$; this behavior of the contact angle is, however, only seen very close to $T_{w,c}$.

In the partial wetting state, upon approach to $T_{w,1}$, the contact angle (almost, but not quite) vanishes as $\theta \sim (T_{w,1} - T)^{1/2}$ as expected for a true first-order wetting transition. In this case, the (effective) exponent of 1/2 is seen already far from $T_{w,1}$.
Fig. 3: Contact angles near the first-order transition for pentane on pure water (thin lines) and for hexane on brine ($c_{NaCl} = 2.5$ mol/L) (thick lines). The solid lines correspond to stable situations, i.e. to partial wetting for $T \leq T_{w,1}$ and to frustrated-complete wetting for $T_{w,1} \leq T \leq T_{w,c}$. The dashed lines indicate metastable extensions of the frustrated-complete wetting state into the region of $T \leq T_{w,1}$, which nevertheless should be observable experimentally due to a pronounced hysteresis [124].

4. Conclusion

It has been shown that the modified Cahn theory, augmented for long-range interactions, which is summarized in Eq. (1), can reproduce the transition temperatures in the sequential wetting of $n$-alkanes on (salt) water [16]. In the present work, we also predict the transition temperatures for pentane on brine as a function of salt concentration, which have not been measured yet. In principle, the theory allows us to calculate the contact angles as well. In practice, however, due to limitations of the precision in the numerical calculation, only the contact angles in the partial wetting state can be determined reasonably reliably. For the frustrated-complete wetting state, we may still estimate the asymptotic behavior of $\theta$ from the contributions of the long-range interactions between substrate and adsorbate alone.

Two of the remaining theoretical tasks are the a priori calculation of the thickness of the depletion layer $\delta$, which we find by matching to the experimentally observed transition temperatures [16], and the ‘ab initio’ calculation of the contact energy, which still has to be obtained from measurements of the surface pressure of the entire system and is, thus, not yet deduced from the properties of the isolated media.

From the experimental point of view, it remains of great interest to see a realization of a critical endpoint, a point at which the line of critical wetting transitions is intercepted by the line of first-order transitions, which will be first-order wetting transitions beyond this point. The discovery of such a system would also demonstrate that the parallelism of the two lines found in the system of hexane on brine is a coincidence rather than a necessity. Measurements of the contact angle in the partial and, particularly, in the frustrated-complete wetting state might be used to test the appropriateness of the present division of the substrate–adsorbate interactions into short-range and long-range forces. The vanishing of the contact angle in
the frustrated-complete wetting state on approach of \( T_{w,c} \) is of primary interested in this respect.

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