

Sequence of Two Wetting Transitions Induced by Tuning the Hamaker Constant

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We report an ellipsometry study of the wetting of hexane on water. By adding salt to the water, we are able to tune the Hamaker constant of this system. This allows us to demonstrate, for the first time, that two rather than one wetting transitions can exist in a single system. Upon increasing the temperature, a discontinuous (first-order) transition from a microscopic film to a mesoscopic film occurs, followed by a continuous (critical) wetting transition that leads to a thick adsorbed film. The latter is due to the Hamaker constant which changes sign with temperature. The first-order transition temperature changes by the same amount as the critical wetting temperature upon changing the Hamaker constant. [S0031-9007(98)06032-3]

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If one considers a liquid droplet on a substrate, in general one distinguishes two possible situations. If the sum of the liquid-substrate and the liquid-vapor interfacial tension is larger than the substrate-vapor interfacial tension, the droplet will have a contact angle between 0° and 180° , a situation called partial wetting. On the other hand, the situation may arise that the sum of the liquid-substrate and the liquid-vapor surface tension equals the substrate-vapor surface tension. The contact angle will then be zero, and the droplet will form a uniform film that covers the whole substrate surface: The liquid completely wets the substrate. The transition between these states, say as a function of temperature, is believed to be a first-order (discontinuous) surface phase transition, as there is a discontinuity in the first derivative of the surface free energy with respect to the temperature [1].

The last few years have seen tremendous progress in the study of these phenomena. For the first time, evidence for the existence of the prewetting line has been obtained in a few systems [2]. Several observations of metastable surface states, such as the discovery of hysteresis in wetting transitions, also underline the generic first-order (discontinuous) character of the wetting transition [2]. On the other hand, Ragil *et al.* recently demonstrated the existence of a counterexample [3]. Studying the wetting behavior of pentane on water, a transition from a mesoscopic (≈ 50 Å) to a very thick film was found that was completely continuous. The possible existence of such a continuous (or *critical*) wetting transition had been disputed for a long time [4]. The conclusion was that it might occur in real systems with long-range interactions, but that these interactions, quantified by the Hamaker constant, should change sign at the critical wetting temperature [4]. It was demonstrated that this was indeed the case for the pentane-water system, and, moreover, it was shown that this is a necessary but not a sufficient condition for critical wetting to occur. Additionally, the system has to be in a state that would show complete wetting in the absence of long-range forces [3].

Ragil *et al.* thus proposed a new scenario for wetting transitions: Instead of two possible surface states (microscopic or macroscopic film) there could be three: An intermediate stage between the two can exist, in which the film is mesoscopic, of the order of several tens of angstroms. This is due to short-range forces that favor wetting, and weak long-range forces (given by the Hamaker constant) that inhibit the formation of a macroscopically thick film. The phase transition picture is then a sequence thin film-intermediate film-thick film, where the first transition is discontinuous and the second is continuous. For the pentane-water system, this suggests that the critical wetting transition should be preceded (at lower temperatures) by a discontinuous transition from a thin to a mesoscopic film. In the experiments, however, no evidence for this transition was found for the lowest temperatures accessible ($T = 0^\circ\text{C}$, below which the water freezes) [3].

For this reason, we report here a study on a slightly different system: the wetting of hexane on (salt) water. We choose hexane since longer alkanes have, in general, higher wetting temperatures [5]. By changing the alkane chain length by one carbon atom, we thus hope to shift the first-order transition to within our experimental window. However, the sad consequence of this is that we also shift the critical wetting transition outside our experimental window. The calculation of the temperature for which the Hamaker constant changes sign (see below), which should be the temperature for which critical wetting takes place, yields $T_{w,c} \approx 100^\circ\text{C}$; the water would be boiling. We thus have to intervene in the Hamaker constant, without changing the first-order transition temperature by too much. This can in fact be achieved by dissolving salt in the water [6]. It is well known that addition of salt changes the polarizability density of the water: It increases the refractive index in the visible light region, and thus brings it closer to the refractive index of hexane. As the Hamaker constant varies practically linearly with the refractive index difference, this allows us to tune the Hamaker constant of the system. As for the first-order

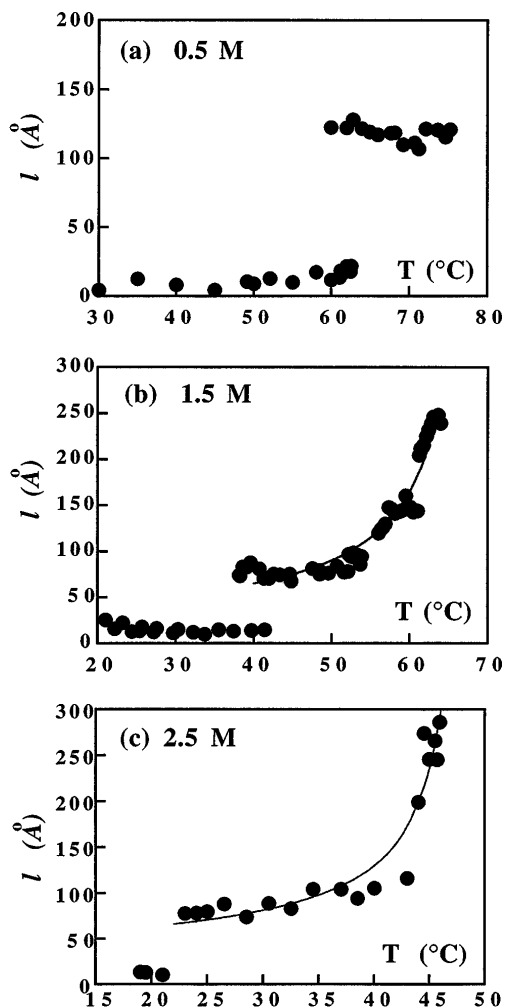


FIG. 1. Measured thickness of the wetting layer as a function of temperature for the three different salinities: (a) 0.5 M, (b) 1.5 M, and (c) 2.5 M NaCl. The drawn lines in (b) and (c) are fits to a power-law divergence of the layer thickness.

transition temperature, measurements of the brine-vapor surface tension and the brine-alkane interfacial tension show that these change with salinity by about the same amount [7]. One may thus—naively—guess that the first-order transition is not shifted too much by the addition of salt.

The measurements were performed on purified water from a Milli-Q-Plus system to which different amounts of reagent grade NaCl were added. Very pure n -hexane ($>99.7\%$) was obtained from Merck and used as received. Thermostating of the cell was performed by inserting it in a copper block through which water from a thermostated water bath was flowing. In order to collect possible lenses of hexane floating around at the surface, a Teflon disk was inserted at one end of the cell. After injection of typically 50 μl of hexane, the cell was flame sealed. The measurements of the wetting film thickness were performed using an ellipsometry technique based on phase modulation described elsewhere [8]. The measured ellipticity can be related, through the Drude formula [9], to the integral over the dielectric constant profile.

As both the brine/hexane and the hexane liquid/vapor interfaces are sharp, we model the hexane layer as a slab with sharp boundaries. This can be done since we are far from any bulk critical point, implying also that the wetting transitions we discuss below are not related to bulk criticality. Finally, to calculate the layer thickness, a background ellipticity of 8×10^{-4} , corresponding to the ellipticity of the bare air-brine interface, is subtracted from the data.

Before discussing the results, it is worthwhile noting that these experiments took a very long time and were very difficult to perform. One reason for this is that the equilibration times are very long. The typical time, after which stable values for the ellipticity are obtained, is on the order of one or two days. A second problem is that the system is very sensitive to external perturbations. This is especially cumbersome since we have to translate the ellipsometry cell in order to verify that the film has a homogeneous thickness over the surface of the water. In addition to this, we also found the system to be very sensitive to temperature gradients. By carefully insulating the whole thermostating system, we arrived at a long-term temperature stability better than 3 mK, which was sufficient to get a stable ellipticity signal.

The results for the thickness of the hexane layer as a function of temperature are shown in Figs. 1(a)–1(c). For the lowest salinity (0.5 M), we observe a clear first-order transition, with a hysteresis, between a microscopic film and a relatively thick—but certainly not infinitely thick—film. Upon increasing the temperature even further, we do not observe an increase in thickness up to the highest temperature that we can reach ($\approx 80^{\circ}\text{C}$) with our thermostating system. Increasing the salinity somewhat more, to 1.5 M, the surprise is that we observe *two transitions*, rather than one. At low T , we start with a microscopic film, typically a few angstroms. Then, around 42°C , we again observe a discontinuous transition to a film that is about 100 \AA thick. Increasing the temperature even further, we observe a layer thickness that diverges continuously, very similar to the critical wetting transition that was reported for the system pentane-water [3]. The same

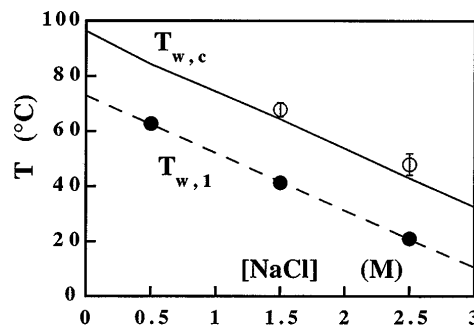


FIG. 2. Wetting temperatures as a function of brine solinity. The drawn line is the result of the calculation of the Hamaker constant: the temperature for which W changes sign. This line coincides with the measured $T_{w,c}$. The dashed line is a linear fit to $T_{w,1}$.

observation is made for the experiment conducted at the highest salinity (2.5 M), only the two transitions appear to be shifted to lower temperatures. In all three cases, the first-order jump is of the order of 100 Å.

As was suggested in Ref. [3], the observed phase-transition sequence can be interpreted as a competition between the short-range interactions and the long-range van der Waals interactions. If, at some temperature, the hexane is favored at the air-water interface by the short-range interactions, the system will tend to form a wetting layer and will do so in a discontinuous way. However, if the Hamaker constant is positive, this will inhibit the film to grow to a large thickness. Thus, this is the usual first-order wetting transition; only the long-range forces inhibit the formation of a thick film. This leads to an intermediate wetting state, sometimes referred to as pseudopartial wetting [10]. If, upon increasing the temperature further, the Hamaker constant will change sign (and thus also favors wetting), the wetting layer thickness will diverge in a continuous way. All of these features are consistent with the experimental results.

For the first-order transition, a hysteresis is observed: Two values of the layer thickness can be found over a certain temperature range. These measurements were performed by starting out from a microscopic film and increasing T until a transition to a mesoscopic film had taken place. The hysteresis was obtained by subsequent cooling; the mesoscopic film persists. Once this mesoscopic film is formed, it is very stable; no transitions to the microscopic film were observed. This agrees with previous observations that it is very difficult to nucleate holes in such a film, which would be necessary to form the microscopic film again [11]. From these arguments, one can infer that the real first-order transition temperature $T_{w,1}$ should be close to the highest temperature for which the microscopic film is still observed.

In order to establish the critical wetting temperature $T_{w,c}$, we have fitted the data to a power-law divergence. The critical wetting transition is due to the vanishing of the Hamaker constant at $T_{w,c}$. If this leading term in the interaction between the two interfaces vanishes, the next-to-leading term becomes important [3,12]. Usually, this term is taken to be positive due to the enhanced density of the wetting fluid near the substrate; in the standard expansion of these forces around the critical wetting temperature, this leads to a divergence $l \sim [T_{w,c} - T]^{-1}$ [3,12]. The fits to the data for the thick film, leaving both $T_{w,c}$ and the power-law exponent as adjustable parameters, are shown in Figs. 1(b) and 1(c). We thus find $T_{w,c}$ and the exponents, which are -0.73 ± 0.11 for 1.5 M NaCl and -0.57 ± 0.19 for 2.5 M NaCl. Thus, contrary to the previous finding for pentane on water [3], we cannot confirm the power-law exponent -1 in this experiment. For the moment, we have no explanation for the discrepancy between these two very similar experimental systems.

The critical wetting temperatures found in this way, $T_{w,c} = 67.9^\circ\text{C}$ (1.5 M) and $T_{w,c} = 48.0^\circ\text{C}$ (2.5 M), should correspond to the temperature for which the Hamaker constant W changes sign. There are two contributions to W that have to be summed [13]. The first is the usual dispersion interaction $W_{\nu>0}$, which contains contributions from all frequencies. The second is the zero-frequency term $W_{\nu=0}$, which depends on the static dielectric constants ϵ_0 . The latter is usually negligible, but, since the dispersion term is small here, it must be retained in the calculation. An exact calculation is difficult due to the complicated dielectric constant of water [5,6,13]. However, an approximate calculation which was shown to work very well for the pentane-water system can be performed [3,13]. In this calculation, one neglects contributions from the infrared and retardation effects and uses the same UV-absorption frequency for all compounds, $\nu_e = 3 \times 10^{15} \text{ s}^{-1}$ [13]. Then, one needs only the static dielectric constant ϵ_0 and the indices of refraction n for visible light. The effect of salt in the water is twofold: It decreases ϵ_0 and increases n of the (salt) water [6,14,15]. It follows from the calculation that both effects lead to a decrease of the total Hamaker constant. The effect of increasing T is similar in the sense that it also leads to a smaller Hamaker constant. This means that, for a given salinity, the overall Hamaker constant changes sign at a certain temperature.

The temperature for which W crosses zero in the calculation is shown, as a function of the salinity, as the drawn line in Fig. 2, together with the critical wetting temperature determined from the experiments. It is observed that the measured $T_{w,c}$ fall practically on the line: The critical wetting transition thus coincides with the temperature for which the Hamaker constant changes sign. The more surprising observation is made when we also consider the results for $T_{w,1}$. With increasing salinity, it is not only $T_{w,c}$ that shifts to lower temperatures, but the first-order transition is shifted by the same amount: *The two transition lines are parallel*. This result is unexpected since, as was already mentioned above, the addition of salt changes the oil-water interfacial tension by about as much as the surface tension of water. As the surface tension of the hexane is unchanged, one would anticipate that the spreading coefficient, and thus the wetting temperature, does not change either. The results thus suggest a direct connection between the observed wetting transitions and the Hamaker constant of the system [13]. This is an important issue, since the prediction of wetting transitions or even surface tensions from intermolecular interaction potentials is notoriously difficult [1,11,16], especially for such complicated molecules as water.

The conclusion that the transition lines are parallel is also in line with the observation that the jump in thickness at the first-order transition is similar for the three different salinities. This jump is expected to diverge if one approaches the critical end point (CEP) where the two transition lines meet [12]; as the lines are parallel,

one would not expect the jump height to change. The measurements on pentane-water show no evidence for a first-order transition for temperatures up to 50 °C below the critical wetting transition: The distance from the critical end point should be larger. For this system, a smaller thickness of the mesoscopic film was found (≈ 50 Å), in accordance with a larger distance from the CEP. From these considerations, one may also anticipate that the critical end point may be obtained by going to larger alkane chain lengths.

For the first-order transition, extrapolation of the data to zero salinity yields $T_{w,1} = 73$ °C for hexane on pure water. This can be compared to our Landau-theory calculation for this system [17], which predicted $T_w = 20$ °C. In this calculation, the long-range forces were not taken into account, and only the first-order transition was found. It thus follows that the theory underestimates the first-order transition temperature by more than 50 degrees. This large discrepancy appears, in fact, to be in line with our experimental observations. As the long-range forces are not included in the theory, and oppose wetting, this should shift the transition to higher temperatures. The observation that the shift is rather large could thus point again to the necessity of taking the long-range forces into account. Independently of the theoretical result, a $T_{w,1} = 73$ °C is consistent with the observations of Mori and co-workers and Pfohl *et al.*, who conclude that the wetting temperature for hexane should be significantly above room temperature [5].

There are two conclusions. First, the wetting behavior of alkanes on water has received much attention, both from the experimental and the theoretical side, because it has important practical applications, e.g., in oil recovery. However, a number of problems remained unresolved so far. Previous work concluded that, at room temperature, short alkanes ($n < 5$) wet water completely, whereas longer alkanes ($n > 6$) exhibit partial wetting. However, for pentane and hexane, the situation was not very clear. The measurements on hexane presented here, when taken together with our previous measurements on pentane, resolve this problem—it follows that at room temperature hexane only partially wets water, whereas pentane is in an intermediate state between partial and complete wetting: pseudopartial wetting.

The second conclusion is that we have demonstrated, for the first time, the existence of two distinctly different wetting transitions rather than one. We can observe the sequence of two transitions by tuning the Hamaker constant of the system. Probably the most important result is that the temperature at which the discontinuous transition takes place changes by the same amount as the critical wetting temperature upon a change in the Hamaker constant W , thus pointing to a direct connection between W and *both* wetting transition temperatures.

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- [1] J.S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Clarendon, Oxford, 1982).
- [2] D. Bonn, H. Kellay, and G.H. Wegdam, Phys. Rev. Lett. **69**, 1975 (1992); J.E. Rutledge and P. Taborek, Phys. Rev. Lett. **69**, 937 (1992); E. Cheng *et al.*, Phys. Rev. Lett. **70**, 1854 (1993); H. Kellay, D. Bonn, and J. Meunier, Phys. Rev. Lett. **71**, 2607 (1993); E. Cheng *et al.*, Rev. Mod. Phys. **65**, 557 (1993).
- [3] K. Ragil, J. Meunier, D. Broseta, J.O. Indekeu, and D. Bonn, Phys. Rev. Lett. **77**, 1532 (1996).
- [4] R. Lipowski and D.M. Kroll, Phys. Rev. Lett. **52**, 2303 (1984); S. Dietrich and M. Schick, Phys. Rev. B **31**, 4718 (1985) observe a similar sequence of wetting transitions (under presumably very similar conditions) for a lattice-gas model; L. Trejo *et al.*, Europhys. Lett. **7**, 537 (1988).
- [5] F. Hauxwell and R.H. Ottewill, J. Colloid Interface Sci. **34**, 473 (1970); C. Del Cerro and G.J. Jameson, J. Colloid Interface Sci. **78**, 362 (1980); S. Akatsuka, H. Yoshigiwa, and Y. Mori, J. Colloid Interface Sci. **172**, 335 (1995); T. Pfohl, H. Moehwald, and H. Riegler (to be published).
- [6] P. Richmond, B. Ninham, and R. Ottewill, J. Colloid Interface Sci. **69**, 45 (1973).
- [7] R. Aveyard and S. Saleem, J. Chem. Soc. Faraday Trans. **73**, 1609 (1977); R. Massoudi and A.D. King, J. Phys. Chem. **79**, 1670 (1976).
- [8] S.N. Jaspersion and S.E. Schnatterly, Rev. Sci. Instrum. **40**, 761 (1969).
- [9] P. Drude, *The Theory of Optics* (Dover, New York, 1959).
- [10] F. Wyart-Brochard *et al.*, Langmuir **7**, 335 (1991); G. Hirasaki, Surf. Sci. Ser. **36**, 23 (1991).
- [11] M. Schick and P. Taborek, Phys. Rev. B **46**, 7312 (1992); R. Bausch and R. Blossey, Phys. Rev. E **48**, 1131 (1993); D. Bonn, H. Kellay, and J. Meunier, Phys. Rev. Lett. **73**, 3560 (1994).
- [12] S. Dietrich, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. Lebowitz (Academic, New York, 1988); S. Dietrich and M. Napiorkowski, Phys. Rev. A **43**, 1861 (1991); V.B. Shenoy and W.F. Saam, Phys. Rev. Lett. **75**, 4086 (1995).
- [13] J.N. Israelachvili, *Intermolecular and Surface Forces* (Academic, London, 1985). The same calculation leads to a prediction of surface tensions solely from knowing the Hamaker constant and using a "universal" cutoff at small length scales; G. Hirasaki, in *Contact Angle, Wettability and Adhesion*, edited by K.L. Mittal (VSP, Utrecht, 1993).
- [14] The refractive index difference was measured using a differential refractometric technique; we find $\Delta n = 0.044\,29 - 0.000\,399\,7T(^{\circ}\text{C})$ for 0.5 M NaCl, $\Delta n = 0.035\,11 - 0.000\,401\,7T$ for 1.5 M and $\Delta n = 0.024\,92 - 0.000\,388\,9T$ for 2.5 M.
- [15] J. Hasted, D. Ritson, and C. Collie, J. Chem. Phys. **16**, 1 (1948).
- [16] However, the short-range interactions involved in wetting transitions can be controlled and quantified; see, for instance, D.J. Durian and C. Franck, Phys. Rev. Lett. **59**, 555 (1987).
- [17] K. Ragil, D. Bonn, D. Broseta, and J. Meunier, J. Chem. Phys. **105**, 5160 (1996).