

Experimental Observation of Critical Wetting

Karine Ragil,¹ Jacques Meunier,² Daniel Broseta,¹ Joseph O. Indekeu,³ and Daniel Bonn²

¹*Institut Français du Pétrole, 1-3 Avenue du bois Préau, F-92500 Rueil-Malmaison, France*

²*Laboratoire de Physique Statistique, Ecole Normale Supérieure, 24, rue Lhomond, F-75231 Paris Cedex 05, France*

³*Laboratorium voor Vaste-Stoffysica en Magnetisme, Katholieke Universiteit Leuven, B-3001 Leuven, Belgium*

(Received 5 April 1996)

An ellipsometry study of the wetting behavior of pentane on water reveals that at a well-defined temperature T_w a continuous transition from a thin to a thick adsorbed film takes place. We present evidence that the transition is due to a Hamaker constant that changes sign with temperature at T_w , and verify that the wetting layer thickness l obeys the power-law divergence, $l \propto (T_w - T)^{-1}$, predicted for critical wetting in systems with van der Waals forces. [S0031-9007(96)00930-1]

PACS numbers: 68.10.-m, 64.70.Ja, 68.45.Gd

The last few years have seen huge progress in the field of wetting phenomena. For the first time conclusive evidence for the first-order nature of wetting transitions, including the discovery of prewetting, has been obtained on a number of systems [1]. This finally confirmed the theoretical predictions of Cahn [2], concerning the first-order (discontinuous) nature of the phase transition.

In contrast, the continuous or *critical* wetting transition has, despite tremendous theoretical attention, so far eluded experimental observation. Theory was partly concerned with short-range critical wetting, for which thermal fluctuations are relevant [3]. For the more realistic van der Waals systems, it was first believed that critical wetting was impossible [4], but subsequent theoretical work has shown that under certain conditions on the long-range forces the phenomenon can occur [5]. More specifically, one needs the Hamaker constant (which describes the net interaction between substrate and adsorbate) to change sign with temperature, a feat that appears hard to accomplish experimentally [6]. Very recent theory, however, predicts critical wetting for a few well-defined systems [7].

In this Letter we present the first observation of a continuous transition between a thin and a thick wetting film of liquid pentane (in contact with its vapor) on water. Besides the importance of critical wetting, the system is itself of interest. The question at which chain length of alkane a transition between partial and complete wetting on water takes place has been much debated [8], as has important practical consequences for, e.g., oil recovery [9]. The current consensus is that alkanes lighter than pentane completely wet water at ambient conditions, whereas longer alkanes wet water only partially. Pentane is a borderline case, and both experimental and theoretical attempts at clarifying the situation have been inconclusive [8,10].

One of the most striking observations is that when droplets of pentane are deposited on water, the final equilibrium state appears to be the coexistence of lenses (droplets) with a thick film [10], in disagreement with the idea that either a molecularly thin or a macroscopic

film should form [2]. However, as these measurements were performed by direct visual observation, no precise information on the thickness of the film was obtained. We therefore set out to measure the equilibrium thickness of films of pentane on water at different temperatures. These measurements were performed in 10 cm long cylindrical closed glass cells that were heated to 550°C before use to remove any organic impurities. Water was taken from a Milli-Q Plus system, and very pure *n*-pentane (>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. All parts of the thermostat were carefully thermally insulated. The temperature was measured to an accuracy of either 10 or 1 mK depending on the required precision. In order to collect possible lenses of pentane floating around at the surface, a teflon disk was inserted at one end of the cell. After injection of typically 60 μ l of pentane and flame sealing the cell, a droplet of pentane in contact with the teflon disk was clearly visible. The thickness of the pentane film was subsequently measured far from the droplet. In the following, the water phase may be considered as an inert “spectator phase” since hardly any pentane dissolves in water (typically 4×10^{-5} g pentane/g H₂O) at the temperatures under consideration.

The film thickness measurements were performed using an ellipsometry technique based on phase modulation described elsewhere [11]. The measured ellipticity can be related, through the Drude formula [12], to the integral over the dielectric constant profile. As both the water/pentane and the pentane liquid/vapor interfaces are sharp (we are far from any critical point), one may model the intruding layer as a slab with sharp boundaries. The ellipticity is then proportional to the layer thickness and the refractive index difference between the two liquid phases. As the index difference is very small, we measured it for our system using a differential refractometric technique. A linear dependence on temperature is found: $\Delta n = 0.03410 - 0.000476T$ (°C).

The primary data of film thickness versus temperature T are depicted in Fig. 1, and appear surprising. At low T a thin (approximately 50 Å) but not molecularly thin film is observed. Upon increasing T , the film thickness increases continuously and appears to diverge around 53 °C. Moreover, the evolution of the thickness with temperature is completely reversible. No difference between heating or cooling cycles was observed. In order to ensure that these values are equilibrium values, we monitored the ellipticity (thickness) in time. Typically, after a change in T of 0.1 °C, the ellipticity would fluctuate over periods of hours, after which a value would be found that remains stable over several days.

The observed continuous growth of the wetting layer over more than an order of magnitude in thickness, together with the absence of hysteresis, makes a strong point that the transition is a continuous or critical wetting transition. A necessary condition for this to occur is that the van der Waals forces change sign. The net interaction between the two interfaces bounding the wetting layer is given by the Hamaker constant W . There are two contributions [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 contains contributions from the dipoles of the water molecules. The latter is usually negligible, but, since the dispersion term is small, it cannot be neglected here. A detailed calculation is difficult due to the complicated dielectric constant of water [10,13]. A rough calculation (neglecting retardation and contributions from the infrared) can be found in Israelachvili's book [13]. To first order, $W_{\nu>0}$ is proportional to the refractive index difference Δn , which changes sign at 71.5 °C. Combining our refractive index measurements with the data of Ref. [13], the calculated Hamaker constant is shown in Fig. 2. It turns out that the two contributions are of opposite sign. The zero-frequency term tends to thicken

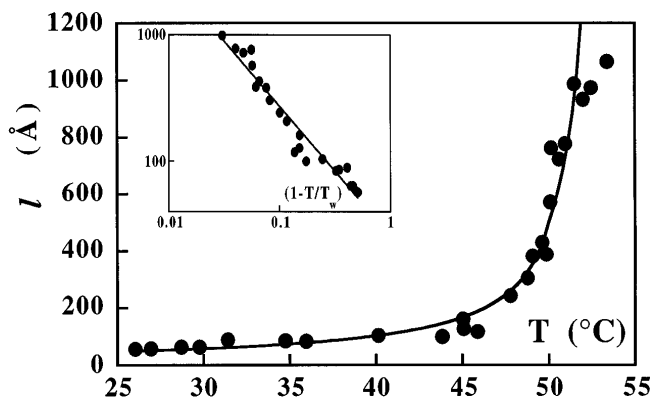


FIG. 1. Measured thickness of the wetting layer as a function of temperature. The drawn line is a fit using the approximate interface potential. Inset: log-log plot of the layer thickness versus the reduced distance from the critical wetting temperature, taking $T_w = 53.1$ °C. The slope of the line is -0.99 ± 0.03 .

the wetting layer, whereas the other term tends to thin it. Moreover, as the dispersion contribution decreases with T , the overall Hamaker constant changes sign at 52 °C.

Thus, the leading term in the interaction between the two interfaces vanishes, which implies that the next-to-leading term becomes important. Usually, this term is taken to be positive due to the enhanced density of the fluid (pentane) near the substrate (water) [7]. Then, in the standard expansion of these forces around the critical wetting temperature [14], the leading term tends to thin the film, and the next-to-leading term tends to thicken it. This leads to the approximate interface potential (i.e., interaction energy per unit area) $V(l) = A/l^2 + B/l^3$, with $A < 0$, $B > 0$. Approaching the critical wetting point T_w , the leading term A varies as $A \propto T - T_w$, so that the layer thickness diverges as a power law, $l \propto B/|A| \propto |T - T_w|^{-1}$. In Fig. 1 we show the fit to the data, with the exponent and T_w as adjustable parameters. This yields $T_w = 53.1 \pm 0.1$ °C and the exponent -0.99 ± 0.03 , which compares favorably to the theoretical prediction of -1 . The wetting temperature is thus found to be very close to the point where the Hamaker constant changes sign, as is indicated by the arrow in Fig. 2. Using the approximate Hamaker constant shown in Fig. 2, the magnitude of the next-to-leading term is found to be 1.3×10^{-31} Jm. This contribution was discussed by Dietrich and Napiorkowski [15], but not evaluated for a specific system.

For the real experimental system under consideration, some reservations should, however, be made. An important point is that for the distances larger than a characteristic absorption wavelength in the ultraviolet, the $W_{\nu>0}$ contribution becomes retarded, i.e., its distance dependence crosses over to l^{-3} . The conclusion should then be that the zero-frequency term is the dominant one at large l and, as it tends to thicken the wetting layer, complete wetting of pentane on water is predicted [13]. This feature indeed shows up in model calculations but turns out

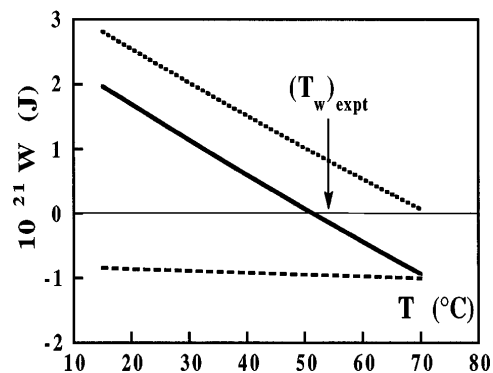


FIG. 2. Calculated Hamaker constants: the zero-frequency contribution (dashed line) tends to thicken the film, whereas the dispersion forces (dotted line) tend to thin it. The overall Hamaker constant (full line) changes sign at 52 °C, very close to the experimentally determined wetting temperature $T_w = 53.1$ °C.

to be extremely weak; it corresponds to a contribution to the disjoining pressure [13] of about 0.2 Pa [10] which would be very hard to observe experimentally. A detailed calculation using Dzyaloshinskii-Lifshitz-Pitaevskii theory [16] is in progress. Second, in our experimental system there is a curved interface, as we collected all the pentane near the teflon disk. This leads to a capillary pressure $\Pi_c = \sigma/R$, where σ is the tension and R the radius of curvature of the water/pentane interface; it follows from the form of the interface (and the fact that we see a finite layer at low temperatures) that Π_c tends to thin the film. However, as we see no (or at most a very small) saturation effect in the layer thickness versus temperature curve for large thicknesses (Fig. 1), this effect is presumably small. In a complete description of the problem, however, it should be taken into account.

To demonstrate experimentally that the observed variation of the layer thickness is indeed due to a variation of the Hamaker constant with temperature, we studied the thickness of adsorbed films off liquid-vapor coexistence of pentane. A new cell was prepared which has two compartments (but no teflon disk), which could be thermostated independently. The first (at $T = T_1$) is filled with water, the second (at $T = T_2$) with pentane. By keeping T_2 just below T_1 , the vapor pressure P of pentane in the two parts is the saturated vapor pressure P at T_2 . By tuning the temperature difference $T_1 - T_2$, we can thus vary P relative to $P_{\text{sat}}(T_1)$ and measure the thickness of the pentane film adsorbed on the water as a function of P/P_{sat} . The difference in temperature translates into a chemical potential distance from coexistence $\Delta\mu = RT \ln P/P_{\text{sat}}$. For T well above T_w (complete wetting), the wetting layer thickness should then behave as $l = (W/6\pi\rho_L\Delta\mu)^{1/3}$ (with ρ_L the density of the liquid pentane) [14] for nonretarded van der Waals forces.

In principle, the measurement of l versus P/P_{sat} then provides a value for the overall Hamaker constant W . In practice, however, one has to go to extremely small temperature differences $T_1 - T_2$ to get a reliable estimate of W . Taking all possible precautions with regard to thermal insulation, we arrived at the results depicted in Fig. 3. Measurements of l as a function of P/P_{sat} are shown below and above T_w . The data for $T < T_w$ show that a thin film is found for all $\Delta\mu$. For $T > T_w$, on the other hand, l increases when $\Delta\mu \rightarrow 0^-$ and appears to diverge very close to coexistence. For the thin film, the data are completely consistent with the interface potential; using the constants determined above, the data are described satisfactorily; also, a steeper increase very close to saturation is predicted. This increase cannot be resolved experimentally, but leads to an intersection with $P/P_{\text{sat}} = 1$ at a thickness of about 100 Å, as was found in the first experiment. For the thick film, on the other hand, the expected divergence occurs further from coexistence than anticipated. The reasons for this apparent discrepancy may be manifold, but a factor that is

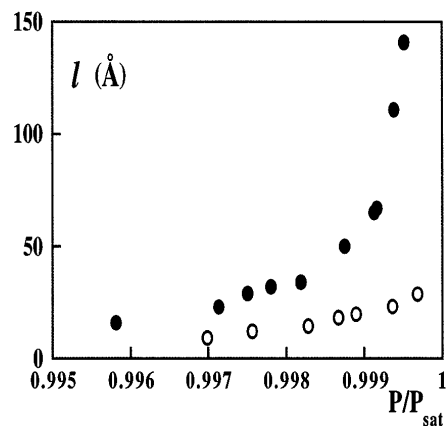


FIG. 3. Film thickness as a function of distance from bulk liquid-vapor coexistence just below and above the wetting temperature: $T = 45^\circ\text{C}$ (open symbols) and $T = 55^\circ\text{C}$ (closed symbols). No “background” contribution for the water/vapor interface was subtracted, so that the baseline is given with an uncertainty of a few Å.

probably very important are the temperature fluctuations in the cell. A small temperature fluctuation which moves the system toward coexistence will lead to a large increase in the layer thickness. A fluctuation in the other direction, on the other hand, will not have a large effect. This has as a consequence that the measured average layer thickness is in fact somewhat higher than expected. Although only qualitatively, for the reasons specified above, these results confirm our earlier assessment. For $T < T_w$ the overall Hamaker constant (neglecting retardation) and $\Delta\mu$ tend to thin the film. Thus, a thin film should be present for all $\Delta\mu$. For $T > T_w$, on the other hand, W tends to thicken the film and the competition with $\Delta\mu$ leads to a diverging layer thickness as $\Delta\mu \rightarrow 0$.

Summarizing, we have presented evidence for a critical wetting transition with a Hamaker constant that changes sign. This, however, turns out to be a necessary but not sufficient condition for critical wetting to occur; it is also necessary that the short-range forces favor wetting. In order to demonstrate this, we consider the phenomenological Landau-Cahn [2] mean-field surface free energy functional $\gamma[m]$, to which we add the effect of the long-range forces. We take [17]

$$\gamma[m] = \int_0^\infty dz \left\{ \frac{1}{2} \left(\frac{dm}{dz} \right)^2 + f(m) - h(z)m \right\} + \varphi_s(m(0)), \quad (1)$$

where z is the distance from the substrate, $m(z)$ the density profile, $f(m)$ the Landau bulk free energy density, φ_s a local surface energy, and $h(z)$ the long-range substrate-adsorbate field. The short-range substrate-adsorbate energy φ_s has been determined previously for this system, using the standard Cahn theory and experimental surface tension data [18]. For that calculation, the long-range forces can be neglected to a first approximation. Setting $h(z) = 0$, one retrieves the standard Cahn argument

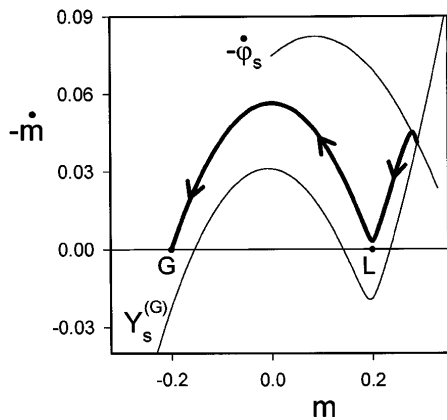


FIG. 4. Phase portrait $\dot{m} = dm/dz$ vs m for the Landau-Cahn model with long-range forces, characterized by $f(m) = (m^2 - m_b^2)^2$, with bulk density $m_b = \pm 0.2$, and $B = 0.15$ and $A = -0.05$. The system is at bulk liquid-vapor coexistence and slightly below the critical wetting point T_w . The thick line gives the computed trajectory for the equilibrium thick film. The computed curve $Y_s^{(G)}$ represents initial conditions for trajectories that end in the gas point G . The intersection of $\dot{\varphi}_s = d\varphi_s/dm$ (derived from experimental input) with $Y_s^{(G)}$ gives the initial condition for the equilibrium profile.

[2]; two local minima for the surface free energy can exist, corresponding to a microscopic and an infinitely thick wetting layer. To account for the long-range forces, we take $h(z) = A/z^3 + B/z^4$, with $B > 0$ and $A \propto T - T_w$, which leads to a similar $V(l)$ as above. The first (local) minimum of $\gamma[m]$ remains practically unchanged, but the minimum corresponding to the infinitely thick wetting film now corresponds to a relatively thick but finite film, as the long-range forces inhibit the layer to grow to infinite thickness. A schematic representation of the results is shown in Fig. 4, together with a computed density profile in the form of a trajectory (thick line) in a phase portrait [2,6]. The trajectory represents the thick (but finite) wetting film. In the limit $A \rightarrow 0^-$ the trajectory touches the bulk liquid point L , which leads to the divergence of the film thickness to infinity. This calculation thus demonstrates that the conditions $B > 0$ and $A \rightarrow 0^-$ are not sufficient for critical wetting to occur. It is also necessary that the intersection of the curve $-\dot{\varphi}_s$ with the computed initial condition curve $Y_s^{(G)}$ occurs sufficiently far to the right in the phase portrait; i.e., the absolute minimum in the surface free energy should be the second one. This means that, for small amplitude B , critical wetting can thus only occur for states which would show complete wetting in the absence of long-range forces. From the figure it follows that this is indeed the case for pentane [18,19].

In conclusion, the data presented above, as well as the theoretical arguments supporting them, provide evidence that the phenomenon we observed is a critical wetting phase transition.

We thank M. Bonn for a critical reading of the manuscript and F. Kalaydjian for his support and interest

in the work. Ecole Normale Supérieure is URA1306 du CNRS, associé aux universités Paris 6 et Paris 7. J.O.I. is supported by the Belgian National Fund for Scientific Research.

- [1] M.R. Moldover and J.W. Schmidt, *Physica* (Amsterdam) **12D**, 351 (1984); D. Bonn, H. Kellay, and G.H. Wegdam, *Phys. Rev. Lett.* **69**, 1975 (1992); J.E. Rutledge and P. Taborék, *ibid.* **69**, 937 (1992); H. Kellay, D. Bonn, and J. Meunier, *ibid.*, 2607 (1993); E. Cheng *et al.*, *Rev. Mod. Phys.* **65**, 557 (1993).
- [2] J.W. Cahn, *J. Chem. Phys.* **66**, 3667 (1977).
- [3] E. Brézin, B.I. Halperin, and S. Leibler, *J. Phys. (Paris)* **44**, 775 (1983); R. Lipowski, D.M. Kroll, and R.P.K. Zia, *Phys. Rev. B* **27**, 4499 (1983); M.E. Fisher and A.J. Jin, *Phys. Rev. Lett.* **69**, 792 (1992).
- [4] M.P. Nightingale, W.F. Saam, and M. Schick, *Phys. Rev. Lett.* **51**, 1275 (1983).
- [5] R. Lipowski and D.M. Kroll, *Phys. Rev. Lett.* **52**, 2303 (1984); S. Dietrich and M. Schick, *Phys. Rev. B* **31**, 4718 (1985).
- [6] P.G. de Gennes, *Rev. Mod. Phys.* **57**, 827 (1985); W. Fenzl, *Ber. Bunsen-Ges. Phys. Chem.* **98**, 389 (1994).
- [7] V.B. Shenoy and W.F. Saam, *Phys. Rev. Lett.* **75**, 4086 (1995); W.F. Saam and V.B. Shenoy, *J. Low. Temp. Phys.* (to be published).
- [8] F. Fowkes, *J. Phys. Chem.* **66**, 2538 (1962); F. Hauxwell and R.H. Ottewill, *J. Colloid Interface Sci.* **34**, 473 (1970); S. Akatsuka, H. Yoshigiwa, and Y.H. Mori, *J. Colloid Interface Sci.* **172**, 335 (1995).
- [9] F. Kalaydjian, J.C. Moulou, O. Vizika, and P. Munkeerud, *Soc. Pet. Eng.* 26671 (1993).
- [10] C. Del Cerro and G.J. Jameson, *J. Colloid Interface Sci.* **78**, 362 (1980).
- [11] S.N. Jasperson and S.E. Schnatterly, *Rev. Sci. Instrum.* **40**, 761 (1969).
- [12] P. Drude, *The Theory of Optics* (Dover, New York, 1959).
- [13] J.N. Israelachvili, *Intermolecular and Surface Forces* (Academic, London, 1985), see also J. Mahanti and B.W. Ninham, *Dispersion Forces* (Academic, New York, 1976).
- [14] S. Dietrich, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. Lebowitz (Academic, New York, 1988).
- [15] S. Dietrich and M. Napiorkowski, *Phys. Rev. A* **43**, 1861 (1991).
- [16] I.E. Dzyaloshinskii, E.M. Lifshitz, and L.P. Pitaevskii, *Adv. Phys.* **10**, 165 (1961).
- [17] V. Privman, *J. Chem. Phys.* **81**, 2463 (1984), and references therein.
- [18] K. Ragil, D. Bonn, D. Broseta, and J. Meunier, *J. Chem. Phys.* (to be published).
- [19] We remark that the mechanism of critical wetting for long-range forces is very different from that for short-range forces. For long-range forces, the curve $Y_s^{(G)}$ becomes degenerate, in the limit $A \rightarrow 0^-$, with the curve $Y_s^{(L)}$, which gives initial conditions for trajectories that end in L . For short-range forces, the curve $\dot{\varphi}_s$ must pass precisely through L for critical wetting to occur.