First-Order and Critical Wetting of Alkanes on Water

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Ellipsometry measurements of the wetting behavior of different alkanes on water show a sequence of two wetting transitions: a first-order (discontinuous) transition followed by a critical (continuous) one. We report temperature-induced wetting transitions for different alkanes and a novel pressure-induced wetting transition for an alkane mixture. The experiments enable us to determine the global wetting phase diagram as a function of chain length and temperature which we subsequently calculate theoretically. The two transition lines are found to be approximately parallel, in accordance with basic theoretical arguments.

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When a liquid droplet is put onto a surface, either one of two equilibrium situations exist, distinguishable by the contact angle θ of the droplet. If the contact angle is zero, the droplet spreads across the surface, a situation known as complete wetting. On the other hand, if the contact angle is between zero and 180°, the droplet does not spread, a situation called partial wetting. The wetting transition from partial to complete wetting is usually of first order [1] and is accompanied by a discontinuous jump in the thickness of the adsorbed film coexisting with the droplet from a microscopic to a macroscopic value. The first-order character of this transition has been demonstrated experimentally by the observation of hysteresis [2].

Wetting transitions which are not first order have been found very recently [3,4]. When n-alkane droplets are deposited on a water substrate, a continuous and reversible divergence of the wetting layer thickness is observed with increasing temperature [5], called a *critical* wetting transition. This divergence is due to a change in sign of the Hamaker constant W, which gives the net effect of the intermolecular van der Waals forces, and represents the difference between alkane-alkane (cohesive) and water-alkane (adhesive) interactions. W changes sign when increasing the temperature, so that the effective attraction between the two surfaces bounding the wetting layer changes to repulsion, leading to the divergence of the layer thickness.

It was demonstrated experimentally that the critical wetting transition is preceded by a first-order transition between a microscopic and a mesoscopic film [6], and that a new wetting state exists between the two transitions, in which droplets coexist with the mesoscopic film. We call this situation *frustrated-complete* wetting. This first-order transition between microscopic and mesoscopic films was anticipated on the basis of a generalization of the Cahn theory of wetting to include the long-range tails which contribute to the Hamaker constant [5,7].

We consider alkanes at the free surface of water. This system has received a lot of attention, although the wetting behavior of the different alkanes is still not clear [8]. One reason for the interest in these systems is that the wetting properties of oil on water in the presence of their common vapor strongly impact oil recovery from water-wet rocks [9]. This is also the reason for studying pressure-induced wetting transitions: it is the pressure one controls in oil recovery.

In this Letter we show that the sequence of two wetting transitions is generic to alkanes and alkane mixtures on water, by determining experimentally the wetting phase diagram for different chain lengths. We consider only short alkanes, as the longer ones are known to crystallize both at free surfaces and on substrates [10]. We subsequently show that it is possible to predict the wetting transition temperatures theoretically, demonstrating how the wetting behavior is related to the intermolecular forces.

The experiments are done by means of ellipsometry measurements [11] of the equilibrium thickness of the liquid alkane film on water. These are carried out in cylindrical closed glass cells half filled with ultrapure water on which a small alkane droplet has been deposited. The film thickness is subsequently measured far from the droplet, which is trapped in a corner of the cell by a Teflon disk [5]. The measured ellipticity is related to the thickness by the Drude formula [12] and is, to a very good approximation, proportional to the layer thickness and to the refractive index difference between the two liquid phases. As the latter is small, we determine it experimentally using differential refractometry for each system.

We first consider the binary alkane mixture of propane (C_3H_8) and hexane (C_6H_{14}). To do ellipsometry at relatively high pressures, we use a cylindrical pressure cell with floating seals [13]. A small quantity (10 μl) of hexane is deposited on the water. Subsequently, the pressure is increased by stepwise injections of gaseous propane. In the following, we mean by pressure the partial pressure of the alkanes.

The experiment shows two pressure-induced wetting transitions (Fig. 1). Upon increasing the pressure, a

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discontinuous jump in the film thickness is observed at $P_{\mathrm{w1}} \approx 3.3$ bars from a microscopic film to a mesoscopic film ($\approx$100 Å). When the pressure is subsequently decreased, the jump in the film thickness takes place at a much lower pressure ($P \approx 1.0$ bar): The system thus exhibits hysteresis. Both this hysteresis and the discontinuous jump clearly show that a first-order wetting transition occurs. For higher pressures, a continuous divergence of the film thickness is observed, which is completely reversible. The divergence, taking place at $P_{\mathrm{cw}} \approx 4.8$ bars, corresponds to a critical wetting transition, similar to that observed for the pentane/water [5] and hexane/brine [6] systems as a function of temperature.

These and previous results [6] suggest that the critical wetting transition found for pentane at 53 °C [5] should also be preceded at lower temperatures by a discontinuous transition from a microscopic to a mesoscopic film. However, Ragil *et al.* found no evidence for this transition by going down to the lowest temperatures accessible experimentally (0 °C) [5]. Repeating the experiment, but starting from a partial wetting state at low temperature (just above 0 °C), we find, surprisingly, that a clear first-order transition takes place at $T \approx 25$ °C (Fig. 2). The conclusion must therefore be that in the experiment of Ragil *et al.* the system remained trapped in a metastable frustrated-complete wetting state, which is extremely long lived [2], so that the thin film state was not observed.

For the wetting of hexane on salt water, the sequence of two wetting transitions has also been observed [6]. The jump at the first-order transition is again of about 100 Å. The dependence of both transition temperatures on salt concentration is found to be linear. Then, the wetting temperatures for hexane on pure water are obtained by extrapolating to zero salt, leading to $T_{\mathrm{w1}} \approx 73$ °C and $T_{\mathrm{cw}} \approx 96$ °C, respectively.

We use the same trick to study the wetting of heptane. Performing measurements as a function of salinity at $T = 20$ °C, the same sequence of two wetting transitions is observed (data not shown). The jump in film thickness at the first-order transition is again of about 100 Å. Extrapolating to zero salinity, assuming parallelism of the transition lines as a function of salt (as found for hexane [6]), yields estimates $T_{\mathrm{w1}} \approx 138$ °C and $T_{\mathrm{cw}} \approx 150$ °C for heptane on pure water.

Knowing the transition temperatures, we can construct the wetting phase diagram (Fig. 3). The lines of first-order and critical wetting transitions separate three regions: partial wetting, frustrated-complete wetting, and complete wetting. To include the pressure-induced wetting transitions in this diagram, we use the so-called equivalent alkane carbon number concept [14]. This gives an effective chain length n_C to a mixture of alkanes, which is the mean chain length of the components weighted by their mole fractions. The two wetting transition pressures of propane/hexane can be related to the composition of the liquid phase using the equation of state discussed below. The composition at 3.3 bars corresponds to an equivalent alkane carbon number $n_{\mathrm{w1}} \approx 4.9$ and that at 4.8 bars corresponds to $n_{\mathrm{cw}} \approx 4.3$. These two new points are consistent with the phase diagram for the pure alkanes, which can thus be extended to alkane mixtures.

The question is now how the wetting behavior can be understood and related to the cohesive and adhesive interactions. We first consider the critical wetting transition. As was predicted theoretically [3] and verified experimentally [5,6], critical wetting occurs through the change in sign of the Hamaker constant W. The interaction between two particles decays with distance r as $u(r) = -(c_{ij}/r^6)$. Integration over the two half spaces bounding a wetting film of thickness l leads to a force per unit area $\prod(l) \approx -(W/l^3)$, with the Hamaker constant $W \approx \pi^2 \rho_{\mathrm{a}}(\rho_{\mathrm{a}} c_{\mathrm{aa}} - \rho_{\mathrm{w}} c_{\mathrm{aw}})$; here ρ_{w} and ρ_{a} are the densities of the water and the alkane, and c_{aw} and c_{aa} are the amplitudes of the alkane-water and alkane-alkane interaction tails [15].

This result was obtained by Hamaker, assuming pairwise additivity of the intermolecular forces. It was shown later that this is not completely justified, although the error is small. The exact expression of the Hamaker constant

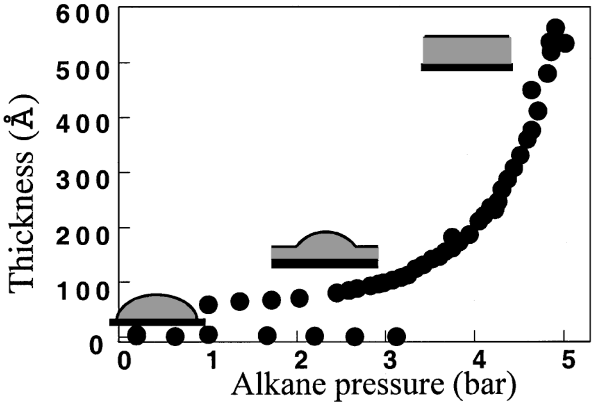

FIG. 1. Measured thickness of the wetting layer as a function of pressure for the propane/hexane system.

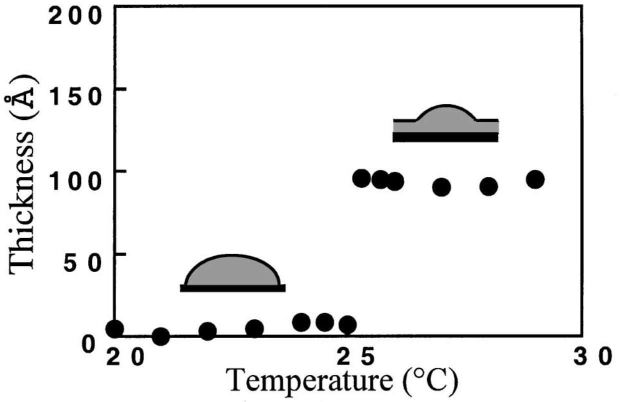

FIG. 2. Measured thickness of the pentane wetting layer as a function of temperature.

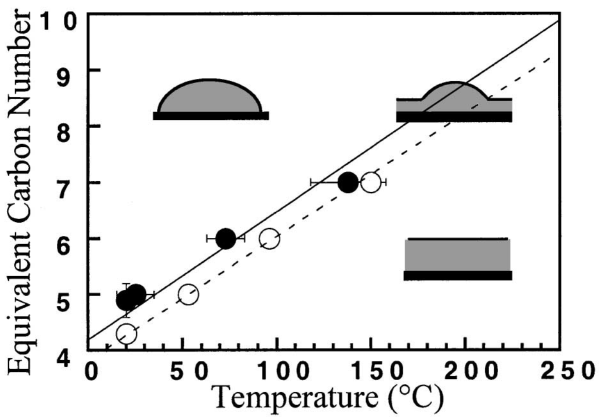

FIG. 3. Global wetting phase diagram: the filled circles correspond to the experimental first-order wetting transitions and the solid line is the theoretically calculated first-order line. The open circles correspond to the experimental critical wetting transitions and the dashed line is the theoretically calculated critical wetting transition line.

[16] is rather complex but can be simplified considerably if retardation effects are neglected and the three media are assumed to possess the same single absorption frequency in the ultraviolet range [17]. Then it effectively decomposes into two contributions: a zero-frequency term arising from dipolar interactions $W_{\nu=0}$ and a dispersion term arising from induced dipoles $W_{\nu>0}$. The former is given by the difference in static dielectric constants, whereas the latter is proportional to the refractive index difference between the water and the alkane phases ($n_{\mathrm{w}} - n_{\mathrm{a}}$). These quantities can still be related to the densities and interaction strengths, so that the Hamaker result can be retrieved approximately. We thus calculate the total Hamaker constant $W = W_{\nu=0} + W_{\nu>0}$, using the measured refractive index difference. The temperature for which W vanishes for each of the alkanes should correspond to the critical wetting temperature and is indeed in excellent agreement with the experimental results (Fig. 3).

It is worth noting here that in the frustrated-complete wetting state the surface free energy is very close to that for complete wetting. The difference can be estimated from the work performed against the disjoining pressure $\prod(l) \approx -(W/l^3)$ between 100 Å and an infinite film, yielding approximately 10^{-6} N m^{-1}, much smaller than a typical surface tension. This allows us to calculate the two wetting transitions independently: Critical wetting follows from the Hamaker constant, whereas first-order wetting follows from the surface tensions. These can be reunited afterwards, by adding the van der Waals interactions as a small perturbation to the surface tension calculation [7].

For predicting the surface tensions, and thus the first-order wetting transitions, it is not feasible to use the molecular interaction potentials directly and solve a microscopic theory. Instead we employ the phenomenological Cahn theory [1,18]. The water is modeled as an impenetrable substrate, and the surface free energy of the substrate-vapor interface is given by an integral involving the concentration profile $\rho(z)$:

$$\gamma(\rho, \rho_\infty) = \int_0^\infty dz \left[\Delta f(\rho, \rho_\infty) + \frac{1}{2} m \left(\frac{d\rho}{dz} \right)^2 \right] + \varphi(\rho_0) .$$

Minimization of this surface free energy yields the equilibrium profile of the adsorbed alkane and thus the wetting state [1]. In the formula, m is the so-called influence parameter [19], ρ_∞ is the density of the vapor, and $\rho_0 = \rho(z = 0)$ is the density at the substrate. Δf represents the local free-energy density of the alkane over that in the equilibrium bulk phase. Δf thus measures the cohesive alkane-alkane interactions and can be deduced from the Peng-Robinson [20] equation of state (EOS):

$$p = \frac{\rho RT}{1 - \rho b} - \frac{a\rho^2}{1 + \rho b(2 - \rho b)} .$$

This EOS is similar to the van der Waals equation; the molar excluded volume b is related to the hard sphere diameter σ through $b/N_a = \frac{2}{3}\pi\sigma^3$, with N_a Avogadro's number [17]; the molar interaction parameter a relates to the amplitude of the cohesive interaction tail through $c_{\mathrm{aa}} = (3/2\pi)^2 ab/N_a^3$.

Adhesive contributions to the surface free energy are included in the Cahn theory through the function $\varphi(\rho_0)$, called a contact energy; usually one assumes an expansion $\varphi(\rho_0) \approx h_1\rho_0 + g\rho_0^2$. For the different alkane-water systems considered here, it was demonstrated recently that this contact energy is a universal function of ρ_0, provided it is rescaled by a factor $\sqrt{mP_c}$, where P_c is the critical pressure of the alkane [21], suggesting that a law of corresponding states operates for the adsorption of alkanes on water, at least as far as $\varphi(\rho_0)$ is concerned.

To quantitatively predict the first-order wetting temperatures, previous attempts used h_1 and g determined from experimental surface tension data. Unfortunately, this led to an underestimation of T_{w1} by more than 50 °C [7,17,21], which is probably a consequence of the assumption that the contact energy depends only on the density exactly at the wall. This assumption also means that Cahn theory does not adequately describe states of low surface adsorption, symptomatic of which is the failure to reproduce Henry's law for thin adsorbed films [22].

Both problems are solved by taking into account the finite width Δz of the first layer of adsorbed alkane, so that the contribution to the free energy in the Cahn theory in the interval $0 < z < \Delta z$ is replaced by a discrete term $\{\Delta f(\rho_0, \rho_\infty) + 1/2m[(\rho_1 - \rho_0)/\Delta z]^2\}\Delta z$, with $\rho_1 = \rho(z = \Delta z)$, and the integral over the density profile runs from Δz to infinity, a thickness domain in which the fully continuum Cahn theory is adequate [22]. In order to minimize the modified surface free energy with respect to the density profile, we choose the hard sphere diameter σ that follows from the EOS as the thickness Δz of the first layer for each alkane (4.1 Å for pentane, 4.4 Å for hexane, and 4.7 Å for heptane). Using these values, the theory yields an adequate prediction for the first-order wetting transitions, as shown in Fig. 3. It is important to stress that this modified-Cahn theory does not make use of any adjustable parameter since the thickness of the first layer is fixed by the size of the molecules.

Also from Fig. 3, the rather surprising observation is that the first-order and critical wetting lines are roughly parallel. That the jump in layer thickness at the first-order transition is approximately the same for all the systems studied lends weight to this observation, since, if the two transition lines were to approach each other, the jump in thickness would increase [23]. The parallelism is interesting, because critical wetting is governed by the tails of the intermolecular forces only, while the first-order transition is governed by both the cohesive interactions featuring in the EOS (also due to the van der Waals forces), and the adhesive forces represented in Cahn theory by the contact energy $\varphi(\rho_0)$. The law of corresponding states for the latter also suggests that it can be related to the total intermolecular interaction potential; the connection, however, still needs some clarification.

A microscopic explanation of the results can be found by examining a density functional theory [24], in which the free energy of the adsorbed alkane is written in terms of an alkane-alkane potential from which the short-range repulsive part is removed, and the alkane-water potential. Short-range repulsion is taken into account by referring the system to a hard-core gas with a molecular volume corresponding to the molar excluded volume b in the EOS, which is proportional to the carbon number n of the alkane. Because the amplitudes of the long-range tails c_{aw} and c_{aa} should be proportional to n and n^2, respectively, it follows that the n dependence of the microscopic functional appears only as a prefactor to the temperature. Thus, the ratio of the temperature of any surface phase transition to the bulk critical temperature T_c would be independent of n, which implies that the transition lines are nearly parallel, as is indeed observed in the experiment.

In conclusion, we performed an experimental determination of the wetting behavior of alkanes on water. Two roughly parallel transition lines exist in the phase diagram, corresponding to first-order and critical wetting transitions. The critical wetting temperatures are well described as the temperatures for which the Hamaker constant changes sign. The first-order wetting temperatures are well described by a modified-Cahn theory.

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