

Sequence of Two Wetting Transitions Induced by Tuning the Hamaker Constant

Noushine Shahidzadeh,¹ Daniel Bonn,¹ Karine Ragil,² Daniel Broseta,² and Jacques Meunier¹

¹*Laboratoire de Physique Statistique, Ecole Normale Supérieure, 24 Rue Lhomond, F-75231 Paris Cedex 05, France*

²*Institut Français du Pétrole, 1-3 Avenue du bois Préau, F-92500 Rueil-Malmaison, France*

(Received 19 September 1997)

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]

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

SEOK, SANGJUN

The van der Waals force between macroscopic solids

1. Microscopic approach (body by body)

$$A_H = \pi^2 C_{AB} \rho_A \rho_B$$

2. Macroscopic calculation – Lifshitz theory

$$A_H \approx \frac{3}{4} k_B T \left(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \right) \left(\frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3} \right) + \frac{3h\nu_e}{8\sqrt{2}} \frac{(n_1^2 - n_3^2)(n_2^2 - n_3^2)}{\sqrt{n_1^2 + n_3^2} \sqrt{n_2^2 + n_3^2} (\sqrt{n_1^2 + n_3^2} + \sqrt{n_2^2 + n_3^2})}$$

e.g. $\varepsilon_1 = \varepsilon_2$ and $n_1 = n_2$ ($\varepsilon_3 = n_3 = 1$), positive (attractive interaction)

By adding salt water



Tuning the Hamaker constant

[14] The refractive index difference was measured using a differential refractometric technique; we find $\Delta n = 0.04429 - 0.0003997T(^{\circ}\text{C})$ for 0.5 M NaCl, $\Delta n = 0.03511 - 0.0004017T$ for 1.5 M and $\Delta n = 0.02492 - 0.0003889T$ for 2.5 M.



first transition (discontinuous)

Table 6.2: Permittivity ϵ , refractive index n , and main absorption frequency ν_e in the UV for various solids, liquids, and polymers at 20°C (Refs [115, 135, 136], handbooks, and own measurements.).

Material	ϵ	n	ν_e (10^{15} Hz)
Al ₂ O ₃ (alumina)	9.3–11.5	1.75	3.2
C (diamond)	5.7	2.40	2.7
CaCO ₃ (calcium carbonate, average)	8.2	1.59	3.0
CaF ₂ (fluorite)	6.7	1.43	3.8
KAl ₂ Si ₃ AlO ₁₀ (OH) ₂ (muscovite mica)	5.4	1.58	3.1
KCl (potassium chloride)	4.4	1.48	2.5
NaCl (sodium chloride)	5.9	1.53	2.5
Si ₃ N ₄ (silicon nitride, amorphous)	7.4	1.99	2.5
SiO ₂ (quartz)	4.3–4.8	1.54	3.2
SiO ₂ (silica, amorphous)	3.82	1.46	3.2
TiO ₂ (titania, average)	11.4	2.46	1.2
ZnO (zinc oxide)	11.8	1.91	1.4
Acetone	20.7	1.359	2.9
Chloroform	4.81	1.446	3.0
<i>n</i> -Hexane	1.89	1.38	4.1
<i>n</i> -Octane	1.97	1.41	3.0
<i>n</i> -Hexadecane	2.05	1.43	2.9
Ethanol	25.3	1.361	3.0
1-Propanol	20.8	1.385	3.1
1-Butanol	17.8	1.399	3.1
1-Octanol	10.3	1.430	3.1
Toluene	2.38	1.497	2.7
Water	78.5	1.333	3.6
Polyethylene	2.26–2.32	1.48–1.51	2.6
Polystyrene	2.49–2.61	1.59	2.3
Poly(vinyl chloride)	4.55	1.52–1.55	2.9
Poly(tetrafluoroethylene)	2.1	1.35	4.1
Poly(methyl methacrylate)	3.12	1.50	2.7
Poly(ethylene oxide)		1.45	2.8
Poly(dimethyl siloxane)	2.6–2.8	1.4	2.8
Nylon 6	3.8	1.53	2.7
Bovine serum albumin	4.0		2.4–2.8

Second transition– PRL 77, 8

Continuous phase transition (T dependence)

Mesoscopic phase

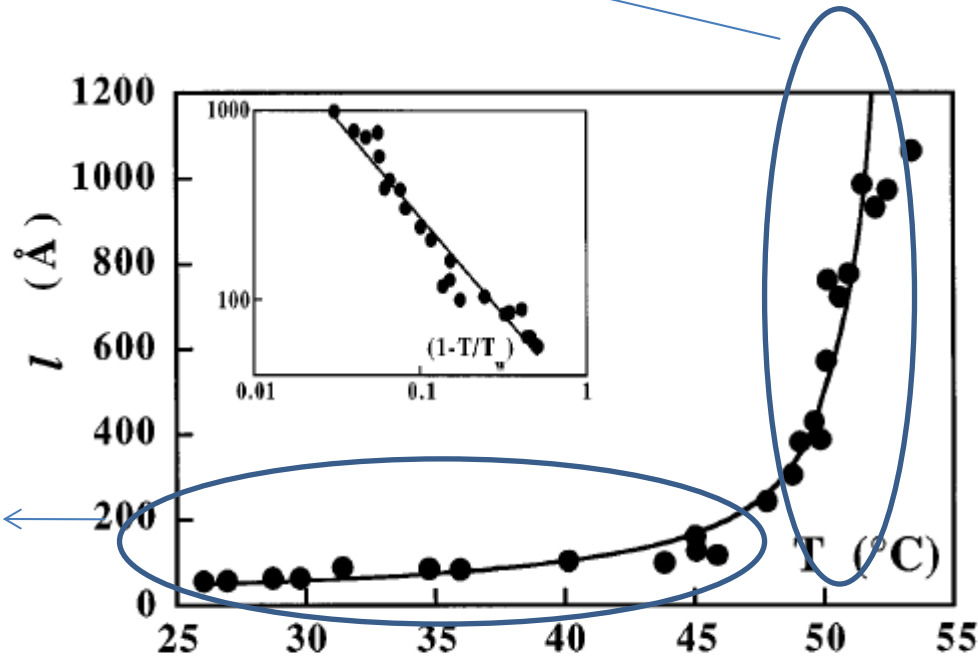


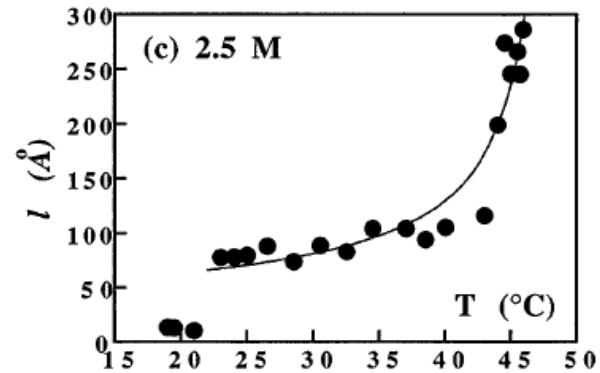
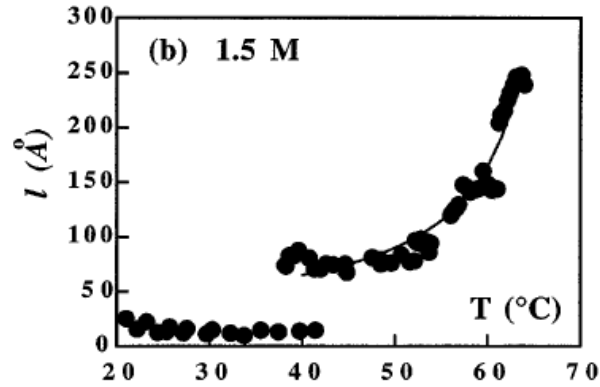
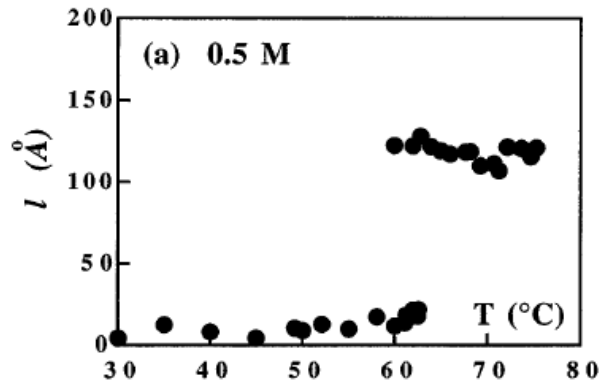
FIG. 1. Measured thickness of the wetting layer as a function of temperature. The drawn line is a fit using the approximate interface potential. Inset: log-log plot of the layer thickness versus the reduced distance from the critical wetting temperature, taking $T_w = 53.1$ °C. The slope of the line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

EXP. method

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 μ l 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.

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.

RESULT



divergence exponent

$$l = [T_{w,c} - T]^{-1}$$



→ -0.73 ± 0.11

→ -0.57 ± 0.19

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.

RESULT

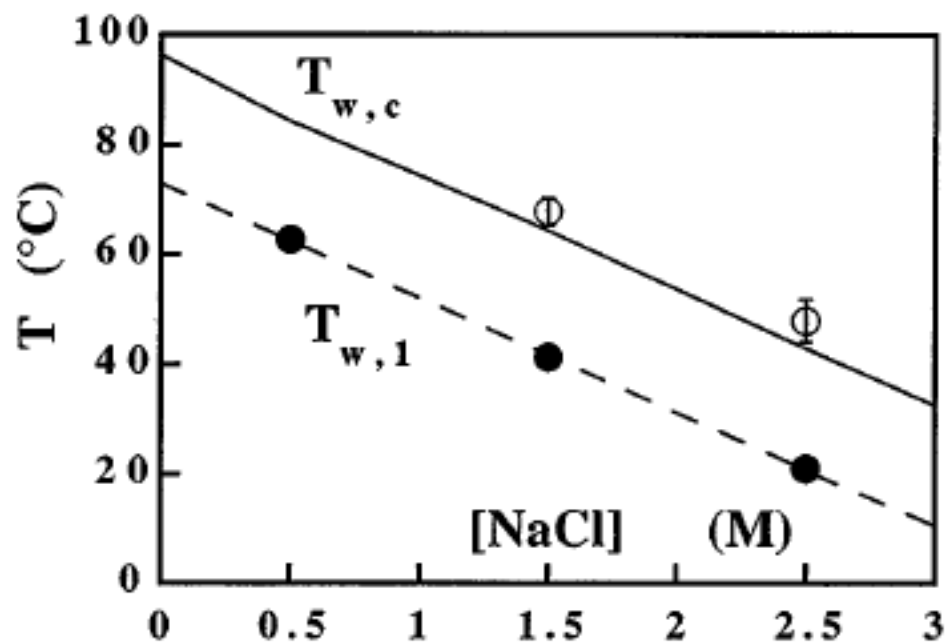


FIG. 2. Wetting temperatures as a function of brine solinity. The drawn line is the result of the calculation of the Hamaker constant: the temperature for which W changes sign. This line coincides with the measured $T_{w,c}$. The dashed line is a linear fit to $T_{w,1}$.