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## Wetting transition for a thin cylinder

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**Résumé.** — Un cylindre de rayon  $b$  immergé dans un mélange binaire A/B produit deux effets : (1) adsorption préférentielle de A, décrite par un champ de surface  $h_1$  ; (2) réduction des interactions A/B près de la paroi (négligée ici). En utilisant la théorie de champ moyen de Cahn, on trouve que le mouillage parfait apparaît seulement pour des cylindres de rayon  $b > b_c(h_1)$ . Près du point critique de démixtion, on trouve un mouillage du cylindre pour des températures  $T > T_w(b, h_1)$ . A  $T_w$ , la transition est du 1<sup>er</sup> ordre. Elle devient du 2<sup>e</sup> ordre pour  $b = b_c$ .

**Abstract.** — A cylinder of radius  $b$  immersed in a two fluid binary mixture A/B produces two effects : (1) preferential adsorption of A, described by a surface field  $h_1$  ; (2) reduction of A/B interactions near the wall (neglected here). Using the Cahn mean-field theory [1], we find that perfect wetting occurs only for cylinders of radius  $b > b_c(h_1)$ . Then near the critical point, wetting is found at temperatures  $T > T_w(b, h_1)$ . At  $T_w$  the transition is first order. It becomes second order when  $b = b_c$ .

### 1. Introduction.

The wetting transition has been extensively studied for plane walls both theoretically [2, 3] and experimentally [4, 5]. Our purpose is to study the case of cylinders which are of both fundamental and practical interest. The wetting of fibers has industrial applications (textile, dyeing, ink...). One can obtain fibers which radii range from several angströms up to macroscopic dimensions.

For *thick fibers*, we must recover the classical 2d behaviour first studied by Cahn [1]. In the simplest model, the effect of the wall just introduces a localized field  $h_1$  describing preferential adsorption. We neglect long range van der Waals forces [6] and the shift of A/B critical temperature induced by the wall [2].

The free energy (per surface site) of the semi-infinite fluid in contact with a planar surface is given by

$$\left. \frac{\Delta F}{kT} \right|_{\text{site}} = -h_1 M_s + \int_0^\infty \left[ \frac{1}{a} \Delta U + \frac{a}{2} (\nabla M)^2 \right] dz \quad (1)$$

where  $M$  is a composition variable ( $M = \phi_A - \phi_B$ ),  $a$  is a molecular size and

$\Delta U = U(M) - U(-M_0)$ , with

$$U = -\frac{1}{2} M^2 \frac{a^2}{\xi^2} + \frac{1}{4} M^4 \quad (2)$$

$(-M_0)$  is the equilibrium composition at infinity  $(M_0 = \frac{a}{\xi})$  and  $\xi = \frac{a}{\sqrt{\frac{T_c - T}{T_c}}}$  is the correlation length.

The minimum of  $\Delta F$  occurs when

$$\frac{d^2 M}{dZ^2} = -\frac{M}{\xi^2} + \frac{M^3}{a^2} \quad (3)$$

with the boundary condition at  $Z = 0$

$$-h_1 = a \frac{dM}{dZ}. \quad (4)$$

Equation (3) describes the motion of a particle in a potential  $-U(M)$ . From (3) and (4) one derives the surface composition  $M_s$  :

$$h_1 = 2 \sqrt{\frac{1}{2} \Delta U(M_s)}. \quad (5)$$

In reduced units  $\frac{M}{M_0} = u$  and  $\frac{Z}{\xi} = X$ , equation (5) leads to

$$\sqrt{2} h_1 \frac{\xi^2}{a^2} = |u^2 - 1|. \quad (6)$$

As shown in figure 1, equation (6) has one or three solutions a, b, c. The stable solution corres-

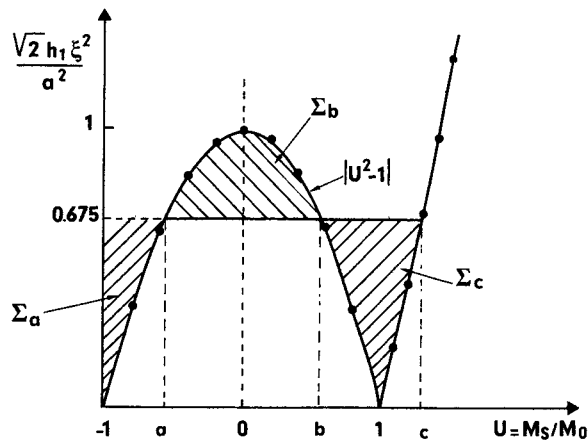


Fig. 1. — Graphic representation of the surface free energy according to Eq. (7'). The bulk fluid composition corresponds to  $u = -1$ . The surface composition is given by the intersection of horizontal lines  $y = \frac{\sqrt{2} h_1 \xi^2}{a^2}$  with the curve  $|u^2 - 1|$  (Eq. (5)). If  $y < 0.675$ , a is the stable root. If  $y > 0.675$ , c is the stable root. If  $y = 0.675$  ( $\Sigma_b = \Sigma_c$ ) there is a first order transition from a to c.

ponds to  $\sigma = \Delta F_{\min}$ . The surface free energy,  $\sigma$ , can be written as :

$$\frac{\sigma}{kT} = + h_1 M_0 + \int_{-M_0}^{M_s} \left[ -h_1 + 2 \sqrt{\frac{\Delta U}{2}} dM \right] \quad (7)$$

i.e.,

$$\frac{\sigma}{M_0 kT} = h_1 + \int_{-1}^{u_s} \left[ -h_1 + \frac{a^2}{\sqrt{2} \xi^2} |u^2 - 1| \right] du. \quad (7')$$

For the roots a, b, c of equation (6), one finds  $\sigma_a - \sigma_0 = k(-\Sigma_a)$ ,  $\sigma_b - \sigma_0 = k(\Sigma_b - \Sigma_a)$  and  $\sigma_c - \sigma_0 = k(\Sigma_b - \Sigma_a - \Sigma_c)$ , where  $\Sigma_i$  are the surfaces defined in figure 1. b corresponds to a maximum. At large  $\xi$ , near the critical point, c is the stable solution (perfect wetting). At low  $\xi$ , a is the stable solution (partial wetting). For  $\xi = \xi_w$  (i.e.,  $T = T_w$ ) we have a first order transition from partial to perfect wetting.  $\xi_w$  is defined by  $\Sigma_b = \Sigma_c$ . It corresponds to  $\sqrt{2} h_1 \frac{\xi_w^2}{a^2} = 0.675$ , i.e.,  $h_1 \frac{\xi_w^2}{a^2} = 2.09$ . The plot of  $\frac{M_s}{M_0}$  versus  $h_1 \frac{\xi^2}{a^2}$  is represented in figure 1.

## 2. Wetting of cylinders.

In the cylindrical geometry, the minimum of  $\Delta F$  is given by

$$a^2 \left[ \frac{\partial^2 M}{\partial r^2} + \frac{1}{r} \frac{\partial M}{\partial r} \right] = -M \frac{a^2}{\xi^2} + M^3 \quad (8)$$

with boundary conditions

$$-h_1 = a \frac{\partial M}{\partial r} \Big|_{r=b} \quad M_\infty = -M_0. \quad (9)$$

In reduced units  $M = M_0 u$  and  $r = \xi X$ , equations (8) and (9) are written as

$$\frac{d^2 u}{dX^2} + \frac{1}{X} \frac{du}{dX} = -u + u^3 \quad (8')$$

$$\frac{du}{dX} \Big|_{X=X_b} = -h_1 \frac{\xi^2}{a^2} \quad \text{or} \quad X^2 \frac{du}{dX} \Big|_{X=X_b} = -h_1 \frac{b^2}{a^2} = -S \quad (9')$$

$$u(\infty) = -1.$$

These equations have been solved numerically. We know a one parameter manifold of solutions for  $X \rightarrow \infty$ ,

$$u = -1 + \frac{e^{-\sqrt{2}(X-\alpha)}}{\sqrt{X}}.$$

We start from a value  $X_0$  of  $X$ . We calculate  $\alpha$  to satisfy  $1 - u(X_0, \alpha) < 10^{-3}$ . We integrate equation (8) and we draw the profiles  $u(X, \alpha)$ . Then we fix a value  $X_b$  of  $X$  and we calculate  $u(X_b, \alpha)$  and  $S = -X_b^2 \frac{du(\alpha)}{dX} \Big|_{X_b}$ . We then plot  $u(X_b)$  versus  $S$  (Fig. 2). We find three different behaviours depending upon the value of  $X$  with respect to  $X_c \simeq 1.8 (\pm 0.1)$  : (1) for  $X_b > X_c$ , there is an S shaped curve (Fig. 2a), i.e. a first order transition for  $S = S_c(X_b)$ .  $S_c(X_b)$  is deter-

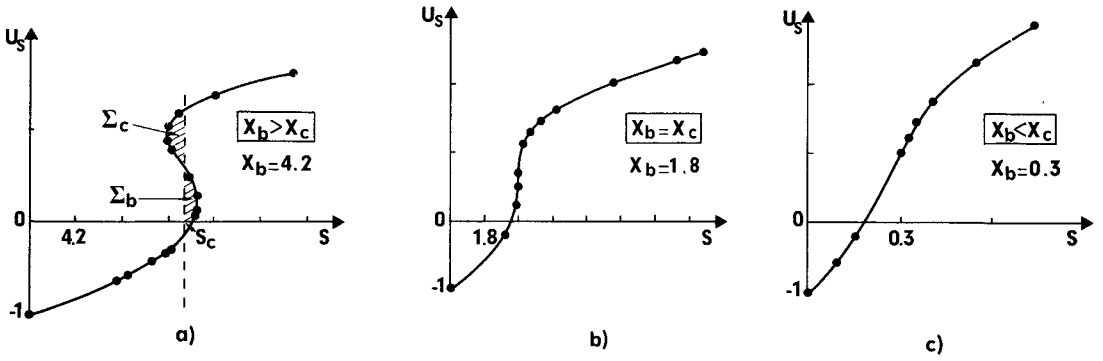


Fig. 2. — Composition at the surface of the cylinder *versus*  $S = h_1 \frac{b^2}{a^2}$  for three reduced radii  $X_b = \frac{b}{\xi}$ : (a) for large cylinders ( $X_b > X_c$ ), we find a first order wetting transition for  $S = S_c$  ( $\Sigma_b = \Sigma_c$ ). (b) for  $X_b = X_c$ , the wetting transition becomes second order. (c) for thin cylinders ( $X_b < X_c$ ), there is no wetting transition.

mined by the equality of the areas  $\Sigma_b$  and  $\Sigma_c$ . (2) for  $X_b < X_c$ , there is no inflexion, i.e. no wetting transition (Fig. 2c). (3) for  $X_b = X_c$ , there is a second order critical point of wetting.

The critical temperature  $T_w(b, h_1)$  is represented in figure 3.  $T_w$  is defined by  $\frac{a^2}{h_1 \xi_w^2} = \frac{X_b^2}{S_c}$  and  $\frac{a^2}{h_1 b^2}$  equals  $\frac{1}{S_c}$ . The curve  $\frac{a^2}{h_1 \xi_w^2}$  *versus*  $\frac{a^2}{h_1 b^2}$  ends up at a second order critical point :

$$\begin{cases} \frac{a^2}{h_1 b_c^2} = 0.17 \\ \frac{a^2}{h_1 \xi_{wc}^2} = \frac{T_c - T_{wc}}{h_1 T_c} = 0.86 . \end{cases}$$

Typically  $\frac{T_c - T_w}{T_c}$  for a plane is of the order of 0.03, i.e.,  $h_1 \simeq 5 \times 10^{-2}$ . This leads to  $\frac{b_c}{a} \simeq 10$ .

It should be noticed that for cylinders the thickness  $z_w$  of the wetting layer is finite, whereas it diverges for a plane surface. For both cases, the first order wetting transition is due to a competition between the two minima of the free energy *versus*  $z_w$ . For the plane, one minimum is at finite  $z_w$  and the other is at *infinite*  $z_w$ . For cylinders, both minima are at finite  $z_w$ . The corresponding composition profiles are shown in figure 4 for the case  $X_b = 4.2$  (Fig. 2a), i.e.  $\frac{b}{a} \sim 16$ . The wetting thickness is of the order of  $\xi$ , i.e. several angströms.

### 3. Conclusion.

Using the most simple description of wetting, we find that a wetting transition appears only for cylinders larger than a critical radius  $b_c$ . This result could possibly be tested by studying the preferential adsorption on a rigid gel of rods of variable size (agarose, collagen, fibrinogen, lectin) swollen by a A/B binary mixture. Even if  $z_w$  is a microscopic length, the surface per unit volume for these systems can be very large and the measured effect can be significant.

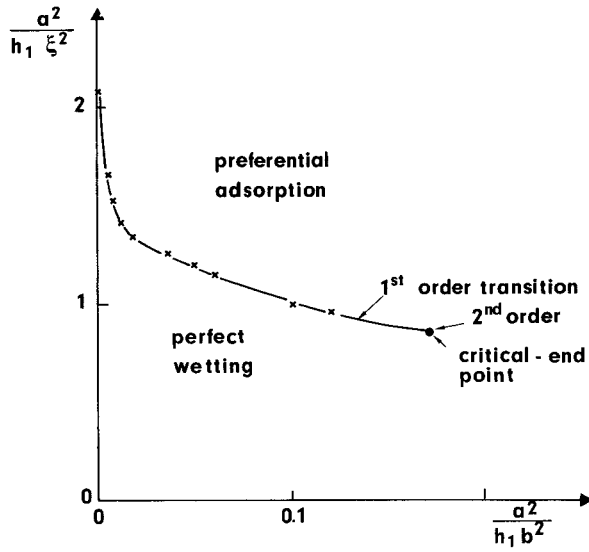


Fig. 3. — Plot of the wetting transition temperature  $\left(\frac{a^2}{h_1 \xi^2} = \frac{T_c - T_w}{h_1 T_c}\right)$  versus  $\frac{a^2}{h_1 b^2}$ . The first order transition line ends at a second-order transition.

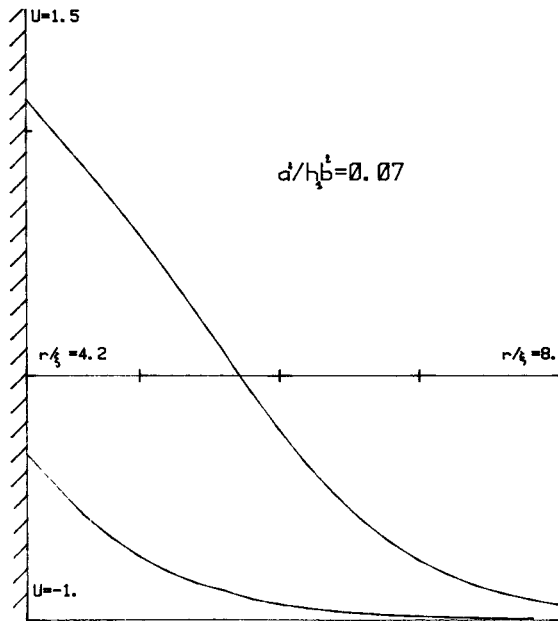


Fig. 4. — Composition profiles just above and below the wetting transition.

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