Eur. J. Mech., B/Fluids, **12,** n° 1, 69-84, 1993

Equilibrium of a Cahn-Hilliard fluid on a wall: influence of the wetting properties of the fluid upon the stability of a thin liquid film

P. SEPPECHER *

ABSTRACT. — A thin liquid film rests on a plane substratum. We study the linear stability of this equilibrium. Usually the stability properties depend upon gravity (as in the Rayleigh-Taylor instability) and not upon the thickness of the film or upon the wetting properties of the fluid. Using the Cahn-Hilliard model for multiphase fluid we show that such influences can be important. These influences decrease exponentially as the film thickness increases and become more important if the gravity is weak and the fluid is close to its critical point.

1. Introduction

We analyze the equilibrium of a thin film of liquid surrounded by its vapor and resting on an infinite plane (cf. *Fig.* 1). If the film of liquid is very thin the interactions between the wall and the liquid-vapor interface may influence the stability of the equilibrium. The description of such interactions depends upon the model used to describe the fluid.

There are no such interactions in the classical theory of capillarity (unless the notion of disjointing pressure is introduced, *i.e.*, long-range forces between the wall and the liquid-vapor interface). Then gravity is then the only parameter which influences the equilibrium governed by the Rayleigh-Taylor instability [Taylor, 1950].

Here, our goal is to study these interactions within the framework of Cahn-Hilliard theory [Cahn-Hilliard, 1959], [Casal, 1972], [Gatignol & Seppecher, 1986]. The Cahn-Hilliard model treats both phases (vapor and liquid) as a single fluid. Its free energy density depends not only on the mass density and the temperature but also on the gradient of the mass density. We will not introduce any long range force.

This model is of mathematical interest (problem of minimizing a surface considered as a limit of a more regular problem [Evans *et al.*, 1992], [Modica, 1987 *b*], study of non-convex functional, application of Γ-convergence [Bouchitte, 1990]). It is also of mechanical importance. As the consistency of this model with the second law of thermodynamics is not obvious, it has been shown that we should add an unusual energy flux into the energy balance equation [Dunn & Serrin, 1985] and that a suitable description of the

* Université de Toulon et du Var, B.P. n° 132, 83957 La Garde Cedex, France.

0997-7546/93/01 69 16/\$ 3.60/

forces in such a fluid is obtainable by using the virtual power principle in the case of the second gradient theory [G & S, 1986], [Germain, 1973]. In this theory the usual stress tensor is no longer sufficient to describe the forces, an additional stress tensor (of order three) is needed. This extra stress tensor is not intuitive in origin. The boundary conditions in second gradient theory are very complex in the general case [G, 1973]. They can be summarized in case of a Cahn-Hilliard fluid on a rigid wall, by the classical stick condition and a second, unusual, condition: the normal derivative of the mass density is to be given on the boundaries [Seppecher, 1989]. The last condition may be viewed as giving information about the interactions between the fluid and the wall. It is connected with the wetting properties of the fluid on the wall: when a liquid-vapor interface is in contact with the wall the contact angle θ formed at the common line is associated with this data [Cahn, 1977], [Modica, 1987 *a*], [S, 1989].

The pratical value of the model is not clear. The exponential convergence of the mass density to its values in the two phases has been criticized [De Gennes, 1985]. The accuracy of the continuum mechanics approximation in thin layers such as interfaces is not clear. This objection is irrelevant when the fluid is close to its critical point [Rowlinson & Widom, 1984]. On the other hand, the coefficients used in the model are not known. For example, the capillarity coefficient λ [*cf.* Eq. (1)] is assumed to be constant since it gives the model mathematical simplicity. Nevertheless this model is the simplest one which describes interfaces.

The dependence of the free energy density upon the gradient of mass density introduces a small characteristic length L (the characteristic thickness of the liquid-vapor interface). It has been shown that, for a fixed domain, the problem of the equilibrium of a Cahn-Hilliard fluid converges, as L tends to zero, to the classical problem of equilibrium with interfaces (The Plateau problem) [M, 1987 *a*]. So, we can expect different phenomena only when this limiting procedure cannot be performed, *i.e.*, if another characteristic length is very small. For example, if the wall is not plane but oscillates with a small wavelength we may expect a hysteresis phenomenon [Bouchitte & Seppecher, 1992], when studying the vicinity of a moving contact line we may expect the removal of the dissipation singularity [Seppecher, 1991]. In the problem we deal with here, we expect some new phenomena when the film is very thin. We emphasize that the study of problems which may predict different results to the classical model of capillarity is the only way to investigate the usefulness of the Cahn-Hilliard model.

In the first section we recall the one-dimensional solution for the equilibrium of a Cahn-Hilliard fluid [C, 1977]. Of the dimensionless variables of this equilibrium, three are especially significant: the first denoted by ε, is the ratio of gravity forces to capillarity strengths inside the interface, the second, denoted by a, is the ratio of the thickness of the liquid film to the thickness of the interface, the last, denoted by μ characterizes the wetting properties of the fluid at the wall. The sign of μ is particularly significant. If μ is positive we will call the fluid a wetting fluid, if μ is negative we will call it a slightly wetting fluid. These two cases correspond to a contact angle smaller or larger than $\pi/2$. The case where μ is close to zero, *i.e.* if the contact angle is close to $\pi/2$, is called the neutral case.

In the second section we study the linear stability of this equilibrium in three cases. In the first case the liquid film is much thicker than the interface ($a=\infty$). We show then that the first approximation for the critical wavenumber is the classical value given by the Rayleigh-Taylor theory. In the two other cases the thickness of the liquid film is finite and there is no gravity. We show that the equilibrium is unstable if $\mu<0$, *i.e.*, if the fluid is slightly wetting. The equilibrium is stable if $\mu>0$. The influence of the wall decreases exponentially as the thickness of the liquid film increases.

In the last part we compare the effects of gravity relative to the effects of the wall. We show that, in usual conditions, and even in micro-gravity conditions, the effects of the wall are insignificant. These effects may only become important for extremely thin (some hundred Angstroms). However, when the temperature is close to the critical temperature of the fluid, these effects may become important even for thick films.

2. The one-dimensional equilibrium

We consider a fluid resting between two infinite plane walls $\{z=-A\}$ and $\{z=B\}$ (*Fig.* 1). At a given temperature the free energy per unit volume of the fluid is:

$$E=W(\rho)+\frac{\lambda}{2}(\nabla\rho)^2 \tag{1}$$

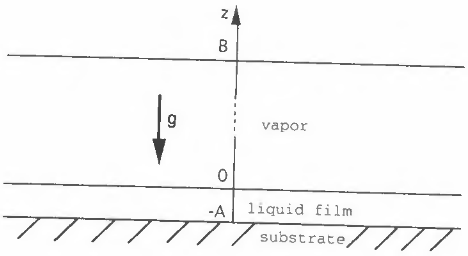

Fig. 1

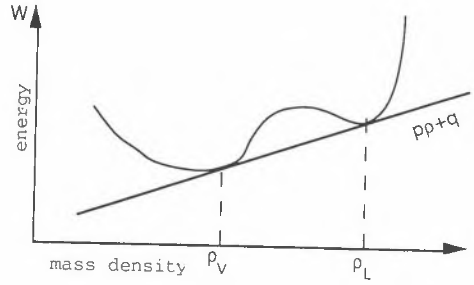

Fig. 2

where ρ is the density of the fluid, $W(\rho)$ is a non convex function (*Fig.* 2) and λ is a coefficient assumed to be a constant (the capillarity coefficient).

The surface energy of the layer is

$$F=\int_{-A}^{B}(W(\rho)+\lambda/2(\nabla\rho)^2+\rho g z)\,dz-m_{-A}\,\rho(-A)-m_B\,\rho(B) \tag{2}$$

where g is the acceleration due to gravity, and m_{-A} et m_B are coefficients related to the wetting properties of the walls.

A one-dimensional equilibrium solution is the function $\rho_e(z)$ which minimizes F, subject to the constraint $\int_{-A}^{B}\rho\,dz=M$.

As we intend only to study the influence of the wall $\{z=-A\}$ upon the equilibrium we assume that $m_B=0$. M is the mass per unit area in the whole layer $\{-A<z<B\}$. This data fixes the thickness of the liquid layer. This mass constraint is needed to obtain the Euler equation associated with the minimization problem (2). Afterwards we will replace it with a given liquid film thickness.

The function ρ minimizing F is a solution of the differential equation

$$\partial W/\partial\rho-\lambda\partial^2\rho/\partial z^2+gz=\text{Const.} \tag{3}$$

where $\int_{-A}^{B}\rho=M$, $\partial\rho/\partial z=-m_{-A}/\lambda$ at $z=-A$ and $\partial\rho/\partial z=0$ at $z=B$.

2.1. The dimensionless quantities and assumptions

Let $\rho\to p\,\rho+q$ be the equation of the bitangent to the graph of the function W (*Fig.* 2) and ρ_v and ρ_L be the values of the mass density at the contact points. We denote by σ the quantity (which is a surface energy):

$$\sigma=\sqrt{2\lambda}\int_{\rho V}^{\rho_L}(W(\rho)-p\,\rho-q)^{1/2}\,d\rho \tag{4}$$

Further, we set $\rho_d=((\rho_L-\rho_V)/2)$ and $\rho_m=((\rho_L+\rho_V)/2)$.

We choose as our characteristic length $L=(\rho_d)^2\lambda/\sigma$ and define the dimensionless quantities

$$x=\frac{z}{L},\quad a=\frac{A}{L},\quad b=\frac{B}{L},\quad u=\frac{\rho-\rho_m}{\rho_d}, \tag{5}$$

$$W=\frac{(W(\rho)-p\,\rho-q)(\rho_d)^2\lambda}{\sigma^2},\quad \mu=\frac{m_{-A}}{2\sigma},$$

$$M_0=\frac{2M}{L\,\rho_d},\quad \varepsilon=\frac{g\,L\,\rho_d^3\lambda}{\sigma^2}$$

The problem is then to minimize the functional

$$f=\int_{-a}^{b}\left(w(u)+\frac{1}{2}u'^2+\varepsilon u x\right)dx-\mu u(-a), \tag{6}$$

such that $\int_{-a}^{b} u\,dx=M_0$,

or to solve the differential equation

$$\frac{\partial w}{\partial u}-u''+\varepsilon x=\text{Const.} \tag{7}$$

with $\int_{-a}^{b} u\,dx=M_0$, $u'(b)=0$ and $u'(-a)=-\mu$,

where u' and u'' denote du/dx and $d^2 u/dx^2$, respectively.

Let u_e be the solution of (7). The intervals where u_e are close to $+1$ or -1 coincide with the liquid and vapor phases, the zone where u_e varies from -1 to $+1$ coincides with the interfacial zone. We study the solutions which correspond to an equilibrium of a liquid film on the wall $\{x=-a\}$. We assume therefore that M_0 is such that the solution u_e is close to $+1$ near the wall $x=-a$ and close to -1 elsewhere (cf. *Fig.* 3 or 4 depending on the sign of μ). We assume that $u(0)=0$ (this is not a restriction since the origin $x=0$ may be chosen to be in the interfacial zone). With this choice for the origin, a and b are no longer free parameters for the problem but unknown quantities. The width $a+b$ of the layer is given but the ratio $a/(a+b)$ is related to the parameter M_0. For large values of a and b we have approximately: $M_0=a\rho_L+b\rho_V$. From now on we will choose a to be a parameter of our problem instead of M_0.

The transition from the value $+1$ to the value -1 occurs in an interval of length of order one. The characteristic length L which we have chosen is the characteristic thickness of the interface.

We shall investigate the influence of the parameters a, μ, ε upon the equilibrium. Here a is the ratio of the liquid film thickness to the interface thickness; generally it is a large quantity; b is the ratio of the vapor phase thickness to the interface thickness. We assume that b is large enough for its influence to be negligible: $b=\infty$ (A finite value for b was necessary only to write the problem in the form (2)). ε is the ratio of the gravitational energy of the interfacial zone to the surface tension: it is a small quantity even in the case of large gravity. Finally μ is the ratio of the surface energy of the wall-liquid interface to the surface tension: this parameter is of order of one. Thus we have

$$b=\infty, \qquad a\gg 1, \qquad \varepsilon\ll 1, \qquad \mu=O(1).$$

2.2. Basic equilibrium solution

Under the conditions of no-gravity and with infinite boundaries ($\varepsilon=0$, $a=b=\infty$, $\mu=0$) it is easy to integrate the Eq. (7) to give

$$x=h(u_0) \quad\Leftrightarrow\quad u_0(x)=h^{-1}(x) \tag{8}$$

where h is the primitive: $h(u)=\int_0^u (2\,w(t))^{-1/2}\,dt$.

This basic solution u_0 satisfies

$$\frac{\partial^2 w}{\partial u^2}(u_0)\,u'_0=u'''_0 \quad \text{[by differentiation of (7)]} \tag{9}$$

and at the boundaries

$$u_0(\pm\infty)=\mp 1, \qquad u'_0(\pm\infty)=0, \qquad u''_0(\pm\infty)=0. \tag{10}$$

The surface energy of the fluid under these conditions is called the (dimensionless) surface tension, denoted by e^s. Its value is 1. This is due to our choice of σ as the characteristic quantity for the energy, σ is actually the surface tension:

$$e^s=\int_{-\infty}^{+\infty}\left(w(u_0)+\frac{1}{2}u_0'^2\right)dx=\int_{-\infty}^{+\infty} u_0'^2\,dx$$

$$e^s=\int_{-1}^{+1}(2\,w(u))^{1/2}\,du=1. \tag{11}$$

2.3. The equilibrium with finite boundaries and no gravity

If $\mu<0$ the equilibrium solution $u_e(x)$ looks like that in Figure 3. There is a maximum in u_e at $x=c\,(u'_e(c)=0)$ $(c<0)$. As the value of a is large but still finite, $u''_e(c)$ is a small,

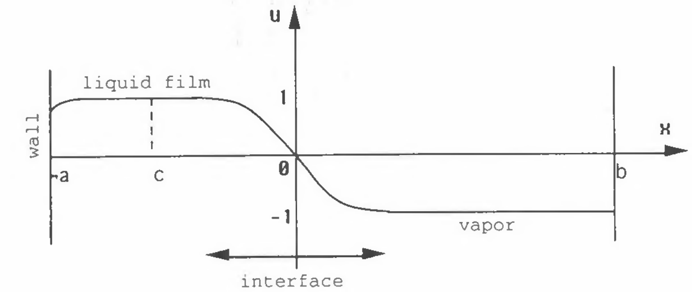

Fig. 3. – The density profile for a slightly wetting fluid.

non zero, negative quantity denoted by v. As b is equal to infinity, we have $u_e(b)=-1$, $u'_e(b)=0$, $u''(b)=0$.

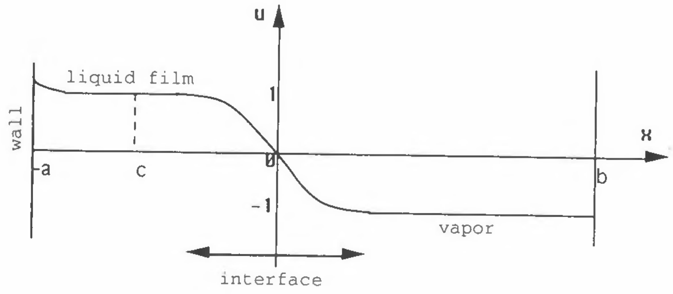

Fig. 4. – The density for a wetting fluid.

If $\mu > 0$ the equilibrium solution $u_e(x)$ is of the type presented in Figure 4. It is a decreasing function with a point of inflexion at $x = c : u_e''(c) = 0\,(c < 0)$. As the value of a is large but finite, $u_e'(c)$ is a small, non zero, negative quantity denoted k. As b is equal to infinity, we have $u_e(b) = -1$, $u_e'(b) = 0$, $u_e''(b) = 0$.

We remark that these descriptions are valid only if μ is not close to zero. If $0 < \mu \ll 1$ the function u_e may have neither a maximum or a point of inflection. Also if $|\mu| = O(1)$ then c is approximately $a/2$ so we have $1 \ll |c|$, $1 \ll a - |c|$.

3. Stability

We study the linear stability of the equilibrium to two-dimensional perturbations. The equilibrium is stable if the variation of the surface energy due to a perturbation which is periodic in the horizontal coordinate is positive for every wavelength. Computing this variation and denoting by $\Phi(x)$ the amplitude of the perturbation, we look for the solutions (α, Φ) of the eigenvalue problem:

$$-\frac{\partial^2 w}{\partial u^2}(u_e)\,\Phi + \Phi'' = -\alpha\,\Phi, \qquad \Phi'(-a) = \Phi'(b) = 0, \tag{12}$$

or, for the value α, for the minimum of the functional:

$$\alpha = \min_{\Phi} \Gamma(\Phi), \qquad \Gamma = \frac{\displaystyle\int_{-a}^{b} ((\partial^2 w/\partial u^2)(u_e)\,\Phi^2 + \Phi'^2)\,dx}{\displaystyle\int_{-a}^{b} \Phi^2\,dx} \tag{13}$$

where $\alpha > 0\,(\alpha < 0)$ means that the equilibrium is stable (unstable).

3.1. The case of infinite boundaries: the Rayleigh-Taylor instability

When the liquid-vapor interface is sufficiently distant from the wall then gravity is the only parameter which influences the stability.

Under conditions of no gravity ($\varepsilon=0$) the equilibrium density $u_0(x)$ is given by the equation (8) and u_0'' is equal to zero at the boundaries. Then the problem (12) has the following simple solution:

$$\alpha_0=0, \qquad \Phi_0(x)=u_0'(x).$$

With gravity small ($0<\varepsilon\ll 1$) we can compute the equilibrium solution as an asymptotic expansion in ε : $u_e=u_0+\varepsilon u_1+\ldots$, u_1 is given by

$$\frac{\partial^2 w}{\partial u^2}(u_0(x))\,u_1-u_1''+x=0. \tag{14}$$

In the same way we look for the solution of the problem (12) as an asymptotic expansion in ε

$$\Phi=\Phi_0+\varepsilon\Phi_1+\ldots, \qquad \alpha=\alpha_0+\varepsilon\alpha_1+\ldots$$

α_1 and Φ_1 are solutions of

$$\frac{\partial^3 w}{\partial u^3}(u_0)\,u_1\,u_0'+\frac{\partial^2 w}{\partial u^2}(u_0)\,\Phi_1-\Phi_1''-\alpha_1\,u_0'=0. \tag{15}$$

By differentiation of (14) we get

$$\frac{\partial^3 w}{\partial u^3}(u_0)\,u_0'\,u_1+\frac{\partial^2 w}{\partial u^2}(u_0(x))\,u_1'-u_1'''+1=0,$$

So that (15) becomes

$$-\frac{\partial^2 w}{\partial u^2}(u_0)\,u_1'+u_1'''-1+\frac{\partial^2 w}{\partial u^2}(u_0)\,\Phi_1-\Phi_1''-\alpha_1\,u_0'=0,$$

and using (9)

$$-u_0'''\,u_1'+u_0'\,u_1'''-u_0'+u_0'''\,\Phi_1-u_0'\,\Phi_1''-\alpha_1\,u_0'^2=0. \tag{16}$$

Integrating this equation from $-\infty$ to $+\infty$ we get

$$[u_0+u_0''\,u_1'-u_0'\,u_1''+u_0'\,\Phi_1'-u_0''\,\Phi_1]_{-\infty}^{+\infty}+\alpha_1\int_{-\infty}^{+\infty}u_0'^2\,dx=0.$$

Finally, using (10) and (11), we have

$$\alpha_1=+2.$$

The first approximation for α is then $\alpha=2\varepsilon$. This is the classical result for Rayleigh Taylor instability: if ε is positive, *i.e.* if g is positive, the equilibrium of the interface is stable. If ε is negative this equilibrium is unstable and the critical wave number n_c is given by: $n_c=(-\alpha)^{1/2}=(-2\varepsilon)^{1/2}$ *i.e.* in dimensional the critical wave number is $\bar{n}_c=n_c/L$

or

$$\bar{n}_c = \frac{(-2\varepsilon)^{1/2}}{L} = \sqrt{\frac{|g|(\rho_L - \rho_V)}{\sigma}}. \tag{17}$$

3.2. THE CASE OF A FINITE BOUNDARY AND NO GRAVITY FOR A SLIGHTLY WETTING FLUID: $m<0$.

Now we study the case $\mu<0$. The equilibrium solution $u_e(x)$ is described in 2.3 where the parameters c and v are also defined.

We denote by $\Phi_0 \in H^1([-a, b])$ the function defined by

$$\Phi_0(x)=0, \qquad \forall x \in [-a, c],$$
$$\Phi_0(x)=u_e'(x), \qquad \forall x \in [c, b].$$

We have

$$\Gamma(\Phi_0) = \frac{\int_c^b ((\partial^2 w/\partial u^2)\Phi_0^2 + \Phi_0'^2)\,dx}{\int_c^b \Phi_0^2\,dx}.$$

Since

$$\int_c^b \left(\frac{\partial^2 w}{\partial u^2}\Phi_0^2 + \Phi_0'^2\right) dx = \int_c^b \left(\frac{\partial^2 w}{\partial u^2} u_e'^2 + u_e''^2\right) dx = \int_c^b (u_e''' u_e' + u_e'' u_e'')\,dx = [u_e'' u_e']_c^b = 0,$$

then $\Gamma(\Phi_0)=0$ and $\alpha \leqq 0$ *i.e. the equilibrium is unstable.*

Let us now search for an approximation to α. Defining $\Psi=\Phi-\Phi_0$, we have

$$\alpha = \min_{\Psi} \frac{\int_c^b ((\partial^2 w/\partial u^2) u_e'^2 + u_e''^2)\,dx + 2\int_c^b ((\partial^2 w/\partial u^2) u_e' \Psi + u_e'' \Psi')\,dx + \int_{-a}^b ((\partial^2 w/\partial u^2)\Psi^2 + \Psi'^2)\,dx}{\int_{-a}^b (\Phi_0+\Psi)^2\,dx}$$

i.e.

$$\alpha = \min_{\Psi} \frac{2\int_c^b (\partial^2 w/\partial u^2\, u_e' \Psi + u_e'' \Psi')\,dx + \int_{-a}^b ((\partial^2 w/\partial u^2)\Psi^2 + \Psi'^2)\,dx}{\int_{-a}^b (\Phi_0+\Psi)^2\,dx}$$

or

$$\alpha=\min_{\Psi}\frac{2\,[u_e''\,\Psi]_c^b=\int_{-a}^{b}((\partial^2 w/\partial u^2)\,\Psi^2+\Psi'^2)\,dx}{\int_c^b u_e'^2\,dx+\int_c^b(2\,u_e'\,\Psi)\,dx+\int_c^b\Psi^2\,dx}. \tag{18}$$

As $a \gg 1$ we have $v \ll 1$ and the function Ψ minimizing the functional (18) is such that $\Psi \ll 1$ [Eq. (22) is an *a posteriori* justification of this assumption]. The first approximation for α is then given by

$$\alpha \cong \min_{\Psi}\frac{-2\,v\,\Psi(c)+\int_{-a}^{b}((\partial^2 w/\partial u^2)\,\Psi^2+\Psi'^2)\,dx}{\int_c^b u'^2\,dx}. \tag{19}$$

Defining $s^2=\partial^2 w/\partial u^2\,(u_e(c))$ and taking a number d such that

$$1 \ll d \ll |c|, \qquad |c+a|, \tag{20}$$

Then u_e is almost constant in $]c-d,\ c+d[$. Therefore $\partial^2 w/\partial u^2\,(u_e)$ is almost constant: $\partial^2 w/\partial u^2\,(u_e) \cong s^2=O(1)$. The function Ψ minimizing the functional decreases exponentially with the distance from c. The distance characterizing this decrease is of order one. We have the successive approximations

$$\alpha \cong \min_{\Psi}\frac{-2\,v\,\Psi(c)+\int_{c-d}^{c+d}(s^2\,\Psi^2+\Psi'^2)\,dx}{\int_c^b u_e'^2\,dx}$$

and

$$\alpha \cong \min_{\Psi}\frac{-2\,v\,\Psi(c)+\int_{-\infty}^{+\infty}(s^2\,\Psi^2+\Psi'^2)\,dx}{\int_c^b u_e'^2\,dx}. \tag{21}$$

The function minimizing (21) is then given by:

$$\begin{cases}\Psi(x)=v/2\,s\,\exp(+s(x-c)), & \text{on } [-\infty,\ c],\\ \Psi(x)=v/2\,s\,\exp(-s(x-c)), & \text{on } [c,\ +\infty],\end{cases} \tag{22}$$

moreover $\int_c^b u_e'^2\,dx \cong \int_{-\infty}^{+\infty} u_0'^2\,dx \cong e^s = 1$ so that

$$\alpha \cong -\frac{v^2}{2s}. \tag{23}$$

We now estimate the value of v. When $u \cong 1$ we have $w(u) \cong s^2(1-u)^2$. Let us denote $u_e(c)-u$ by δ. When $\delta \cong 0$, δ is given by the differential equation

$$\frac{\delta'^2}{2} = \frac{s^2\delta^2}{2} + v\,\delta. \tag{24}$$

Its solution has the following form:

$$\delta(x) = \frac{v}{s^2}(\mathrm{ch}(s(x-c))-1). \tag{25}$$

When $|\mu|$ is of order one we have $-c \cong a+c \cong a/2$, so δ is of order one at the wall and in the liquid-vapor interface. Thus we have

$$\frac{v}{s^2}\left(ch\left(\frac{sa}{2}\right)-1\right) = O(1)$$

with $v \ll 1$, $a \gg 1$, $s = O(1)$. Also

$$v = O\left(2s^2 \exp\left(-\frac{sa}{2}\right)\right). \tag{26}$$

$$\alpha = O(-2s^3 \exp(-sa)). \tag{27}$$

In order to write (27) interms of dimensional quantities, let us introduce $\bar{\alpha} = \alpha/L^2$ and S the speed of sound in the liquid phase: $S^2 = \rho_L(\partial^2 W/\partial\rho^2)(\rho_L) = s^2(\rho_L\sigma^2/\rho_d^4\lambda)$. We have

$$\bar{\alpha} = -O\left(\frac{2\rho_d^2 S^3}{\sigma\lambda^{1/2}\rho_L^{3/2}} \exp\left(-\frac{S}{\lambda^{1/2}\rho_L^{1/2}}A\right)\right). \tag{28}$$

3.3. The case of a Finite boundary and no gravity for a wetting fluid: $m>0$.

Now we study the case $\mu>0$. The equilibrium solution $u_e(x)$ is described in 2.3 where the parameters c and k are also defined. We denote by $\Phi_0 \in H^1([-a, b])$ the function defined by

$$\Phi_0(x) = k, \qquad \forall x \in [-a, c],$$
$$\Phi_0(x) = u_e'(x), \qquad \forall x \in [c, b].$$

As in the previous case let us take $\Phi = \Phi_0 + \Psi$:

$$(29)\quad \alpha = \min_{\Psi} \left\{ \left[\int_{-a}^{c} \left(\frac{\partial^2 w}{\partial u^2} k^2 \right) dx + 2 \int_{-a}^{c} \left(\frac{\partial^2 w}{\partial u^2} k \Psi \right) dx + \int_{c}^{b} \left(\frac{\partial^2 w}{\partial u^2} u_e'^2 + u_e''^2 \right) dx + 2 \int_{c}^{b} \left(\frac{\partial^2 w}{\partial u^2} u_e' \Psi + u_e'' \Psi' \right) dx + \int_{-a}^{b} \left(\frac{\partial^2 w}{\partial u^2} \Psi^2 + \Psi'^2 \right) dx \right] \left[\int_{-a}^{b} (\Phi_0 + \Psi)^2 \, dx \right]^{-1} \right\},$$

however

$$\int_{c}^{b} \left(\frac{\partial^2 w}{\partial u^2} u_e'^2 + u_e''^2 \right) dx = [u_e'' u_e']_c^b = 0,$$

and

$$\int_{c}^{b} \left(\frac{\partial^2 w}{\partial u^2} u_e' \Psi + u_e'' \Psi' \right) dx = [u_e'' \Psi]_c^b = 0,$$

and

$$\int_{-a}^{b} (\Phi_0 + \Psi)^2 \, dx \cong \int_{-a}^{b} (u_e')^2 \, dx \cong e^s = 1,$$

so

$$(30)\quad \alpha = \min_{\Psi} \left\{ \left(\int_{-a}^{c} \left(\frac{\partial^2 w}{\partial u^2} k^2 \right) dx + 2 \int_{-a}^{c} \left(\frac{\partial^2 w}{\partial u^2} k \Psi \right) dx + \int_{-a}^{b} \left(\frac{\partial^2 w}{\partial u^2} \Psi^2 + \Psi'^2 \right) dx \right\}$$

The function Ψ minimizing this functional decreases exponentially with distance c in $[c, b]$ and $\Psi + k$ decreases exponentially with distance from c in $[-a, c]$. The characteristic distances for the decrease is of order one [*cf.* Eq. (32)].

With the same notation as in (20), (21) we have

$$\alpha \cong \min_{\Psi} \left\{ \int_{c-d}^{c} \left(\frac{\partial^2 w}{\partial u^2} (\Psi + k)^2 + (\Psi + k)'^2 \right) dx + \int_{c}^{c+d} \left(\frac{\partial^2 w}{\partial u^2} \Psi^2 + \Psi'^2 \right) dx \right\}$$

i.e.

$$(31)\quad \alpha \cong \min_{\Psi} \left\{ \int_{-\infty}^{c} (s^2 (\Psi + k)^2 + (\Psi + k)'^2) + \int_{c}^{+\infty} (s^2 \Psi^2 + \Psi'^2) \right\}$$

The function minimizing (31) is then given by

$$(32)\quad \begin{cases} \Psi(x) = -k/2\,(2 - \exp(+s(x-c))) & \text{in } [-\infty, c] \\ \psi(x) = -k/2 \exp(-s(x-c)) & \text{in } [c, +\infty] \end{cases}$$

(33) $$\alpha \cong \frac{sk^2}{2}$$

We now estimate k. With the same notation as in (24), when $\delta \cong 0$, δ is given by the differential equation

(34) $$\delta'^2 = s^2 \delta^2 + k^2.$$

The solution has the following form:

(35) $$\delta(x-c) = \frac{k}{s} sh(s(x-c)).$$

When μ is of order one we have $-c \cong a + c \cong a/2$, so that δ is of order one at the wall and in the liquid-vapor interface. Thus

$$\frac{k}{s} sh\left(\frac{sa}{2}\right) = O(1) \quad \text{with } k \ll 1,\ a \gg 1, \qquad s = O(1).$$

Also

(36) $$k = O\left(2s \exp\left(-\frac{sa}{2}\right)\right)$$

and

(37) $$\alpha = O(2s^3 \exp(-sa))$$

i.e. in dimensional terms

$$\bar{\alpha} = O\left(2\frac{s^3}{L^2} \exp(-sa)\right)$$

or

(38) $$\bar{\alpha} = O\left(\frac{2\rho_d^2 S^3}{\sigma \lambda^{1/2} \rho_L^{3/2}} \exp\left(-\frac{S}{\lambda^{1/2} \rho_L^{L/2}} A\right)\right).$$

3.4. THE CASE OF A FINITE BOUNDARY AND NO GRAVITY FOR THE NEUTRAL CASE $m \cong 0$

If $|\mu| \ll 1$ the approximations (26) and (36) are no longer appropriate.

When $\mu = 0$, the density profile u_e has a maximum when $x = -a$. The computations are similar to those in 3.2. The approximations (21) and (26) are suitably modified and we get the approximation:

(39) $$\alpha \cong -O(4s^3 \exp(-2sa))$$

We now calculate the value of μ for which $\alpha=0$. If $\alpha=0$ the solution of (12) is $\Phi=u_e'$. Then $u_e''(-a)=0$ and the density profile has a point of inflexion at $x=-a$. $u_e'(-a)=k=-\mu$, where k may be estimated in the same way as led to (34), (35), (36). We get the approximation

$$\mu \cong O(2s \exp(-sa)). \tag{40}$$

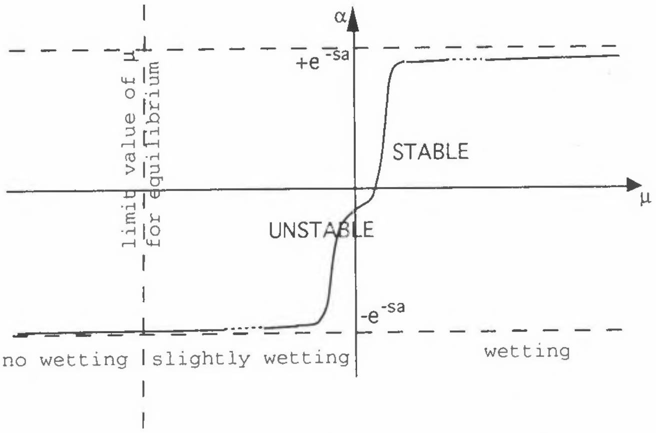

Fig. 5. – The influence of the wetting properties of the fluid upon its stability.

These results are recorded in Figure 5. We notice that outside of the vicinity of the zero, the actual value of μ is unimportant, the important parameter is the sign of μ.

4. A comparison of gravitational effects with wall proximity effects

4.1. The case of pure water in ordinary conditions or in micro-gravity conditions

We use the units of internal capillarity (U.C.I.) defined in [Casal & Gouin, 1988]: the length unit is 5×10^{-10} m, the mass unit is $1,5 \times 10^{-25}$ kg, and the time unit is 7×10^{-13} s.

Following the computation by [C & G, 1988], using a van der Waals function for W, we get:

$$\left\{ \begin{array}{lll} \lambda = 1\,\text{U.C.I.}; & \sigma = 0.22\,\text{U.C.I.}; & \rho_d = 0.5\,\text{U.C.I.}; \\ L = 1\,\text{U.C.I.}; & g = 10^{-14}\,\text{U.C.I.}; & S = 1.4\,\text{U.C.I.}; \\ & \varepsilon = 2 \times 10^{-14}. & \end{array} \right. \tag{41}$$

The wall proximity effects are comparable with the gravitational effects when the liquid film thickness is of order of $L/S\,|\text{Ln}(\varepsilon)|$ *i.e.* when

$$A = O(22\,\text{U.C.I.}) = O(110\,\text{Å}).$$

We emphasize that the effects of the proximity of the wall are weak in the case of liquid films of ordinary thickness. This result is true even in microgravity conditions:

For example, if the gravity is 10^{-6} g we have

$$\varepsilon = 2\times 10^{-20}; \qquad A = O(31\ \text{U.C.I.}) = O(160\ \text{Å})$$

We remark that the use of continuum mechanics in such thin films is typical for the Cahn-Hilliard model and has already been discussed in the introduction.

4.2. THE VICINITY OF THE CRITICAL POINT

We follow here [Rowlinson & Widom, 1984]. These authors studied interfaces in the vicinity of the critical point. Every parameter of the fluid depends upon the "distance from the critical point": $T - T_c$. (Where T_c denotes the critical temperature of the fluid). The results of [R& W, 1984] are

$$(42) \qquad \rho_L - \rho_V \sim |T - T_c|^{\beta}; \qquad \frac{\partial^2 W}{\partial \rho^2}(\rho_L) \sim |T - T_c|^{-\gamma}; \qquad \sigma \sim |T - T_c|^{\gamma - \nu + 2\beta}.$$

Thus, for the quantities we have defined,

$$(43) \quad S \sim |T - T_c|^{-\gamma/2}; \qquad L \sim |T - T_c|^{-\nu}; \qquad \varepsilon \sim |T - T_c|^{-\nu - \beta - \gamma}; \qquad s \sim |T - T_c|^{0}.$$

The maximum film thickness for which the wall effects are substantial is

$$A \sim \frac{L}{s} \operatorname{Ln}(\varepsilon) \sim |T - T_c|^{-\nu} \operatorname{Ln}(|T - T_c|).$$

The exponents are, according to mean field theory, $\beta = 1/2$, $\gamma = 1$, $\nu = 1/2$, but are actually [R & W, 1984] closer to

$$\beta = 0.32; \qquad \gamma = 1.24; \qquad \nu = 0.63.$$

The thickness A therefore diverges at the critical temperature. Moreover it diverges faster than does the characteristic thickness of the interface.

The wall effects which are negligible in usual conditions, may become very important when gravity is weak and when the temperature is close to the critical temperature.

There is some uncertainty about these results. The approximations (12)-(17) we used are accurate if $\varepsilon \ll 1$. But ε diverges at the critical temperature [*see* (43)]. We must therefore assume that some value of the temperature exists such that both approximations $\varepsilon \ll 1$ and (43) are valid.

On the other hand the model we use to describe the fluid is a very simple one which does not take into account long-range interactions. The exponential decrease of the wall's influence is a characteristic phenomenon for this model. It is associated with the exponential convergence of the density to the density in the phases, and this exponential convergence has been criticized [De G, 1985].

Acknowledgement

This study has been supported by the Centre National d'Études Spatiales. (Contract N° 91/C.N.E.S./0234.)

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(Manuscript received February 19, 1992;
accepted July 25, 1992.)