

Boundary effects in phase transitions

G. ALBERTI, G. BOUCHITTÉ, P. SEPPECHER

Abstract: We study the asymptotic behaviour of Cahn and Hilliard model under the assumption that the boundary surface energy is a two-wells positive function very large for intermediate values. We show that the limit energy is non local, taking into account boundary surface phases. When these phases coincide with the trace of the volume phases, the limit energy is the classical capillary energy with an extra term corresponding to line tension.

1. – Introduction

An usual way to study multiphase materials is to consider homogeneous phases separated by bidimensional interfaces of constant surface tension. The contact angle of these interfaces with the boundary of the container is prescribed and depends on the boundary surface energies through the so-called Young's law [7]. Sometimes, an energy per unit length concentrated on the contact line (line tension) is added to the model [10]. This paper is an attempt to show that the classical Cahn and Hilliard model can lead mathematically to such a line tension.

The model of Cahn and Hilliard [4] is the simplest continuum model for phase transition: the total energy of a fluid whose mass density is denoted u is the sum of a non convex volume energy $W_1(u)$ and of a term $\lambda |Du|^2$ taking into account the non homogeneity of the fluid. The function W_1 is a two-wells positive function vanishing only for $u \in \{\alpha_1, \beta_1\}$. The coefficient λ (capillarity coefficient) introduces an intrinsic length (characteristic of the thickness of an interface). As this length is in general much smaller than the characteristic length of the container, a small parameter ε appears. The equilibrium of such a fluid can be studied in an asymptotic way. This has been done by Modica [9] who considered the Γ -convergence of the functional

$$(1.1) \quad F_\varepsilon(u) := \varepsilon \int_\Omega |Du|^2 + \frac{1}{\varepsilon} \int_\Omega W_1(u) + \int_{\partial\Omega} \sigma(Tu)$$

Here $\sigma(Tu)$ is the surface energy on the boundaries of the container and Tu denotes the trace of u . Under the implicit assumption that $\sigma(Tu)$ is of order ε^0 , L. Modica proved that going to the limit $\varepsilon \rightarrow 0$ the resulting model is the classical one with constant surface tension, constant surface energies on the boundary of the domain.

The contact angle predicted by Young's law is recovered. Indeed the limit of F_ε is given by:

$$(1.2) \quad F_0(u) := c_1 \mathcal{H}^{N-1}(\partial A \cap \Omega) + \widehat{c}_1 \mathcal{H}^{N-1}(\partial \Omega \cap A)$$

if u is equal to α_1 inside A and to β_1 outside. The coefficients c_1 and \widehat{c}_1 in (1.2) are explicitly determined by W_1 and σ (see [9]). Cahn and Hilliard model leads to qualitatively correct predictions although it does not take into account any long range forces near the boundary $\partial \Omega$ (the importance of these forces is well known for boundary effects in phase transition [5]).

A lot of variants of problem (1.1) can be considered by assuming different behaviors for every quantity with respect to ε . A first variant was described in [3] where we considered a wall with roughness of order ε (in this case Ω depends upon ε) and, using homogenization techniques, we made explicit the dependence of the contact angle on the roughness parameters of the boundary.

The variant we propose in this paper is quite new: it rests upon the observation that a concentration of energy appears in the vicinity of the contact line where the trace of u_ε (a minimizer of F_ε) differs from its values far away on the wall. So we choose a surface energy which becomes very large for intermediate values: σ in (1.1) is replaced by $\lambda_\varepsilon W_2$ where W_2 is a positive two-wells function vanishing only on $\{\alpha_2, \beta_2\}$ and λ_ε is a parameter tending to infinity with a appropriate scaling. Then we study the asymptotic behaviour of the following functional:

$$(1.3) \quad F_\varepsilon(u) := \varepsilon \int_\Omega |Du|^2 + \frac{1}{\varepsilon} \int_\Omega W_1(u) + \lambda_\varepsilon \int_{\partial \Omega} W_2(Tu)$$

expecting a limit energy generalizing (1.2):

$$(1.4) \quad F_0(u) := c_1 \mathcal{H}^{N-1}(\partial A \cap \Omega) + \widehat{c}_1 \mathcal{H}^{N-1}(\partial \Omega \cap A) + c_2 \mathcal{H}^{N-2}(\partial A \cap \partial \Omega)$$

where the coefficient c_2 represents the line tension. Unfortunately F_0 cannot be the limit in the sense of Γ -convergence since it is not lower semicontinuous with respect to $L^1(\Omega)$ -convergence. The point is that the limit v of the trace of u may not coincide with the trace of the limit of u . From a mechanical point of view, a surface phase separation appears on the boundary ($v \in \{\alpha_2, \beta_2\}$) and the dividing line Sv does not necessarily coincide with the contact line (i.e. the trace of the interface Su on the boundary $\partial \Omega$, see Fig. 2).

Our result (theorem 2.1) takes into account this possible dissociation between surface and volume phases and brings to the fore the interesting scaling for λ_ε :

$$(1.5) \quad \lim_{\varepsilon \rightarrow 0} \varepsilon \log \lambda_\varepsilon = K \in]0, +\infty[$$

which ensures the relative strong compactness in $L^1(\partial \Omega)$ of the traces Tu_ε under the equiboundedness assumption of energies $F_\varepsilon(u_\varepsilon)$. Moreover we show that F_ε considered as a functional of the pair (u, Tu) converges to a function $\Phi(u, v)$ defined for $(u, v) \in BV(\Omega, \{\alpha_1, \beta_1\}) \times BV(\partial \Omega, \{\alpha_2, \beta_2\})$ by:

$$(1.6) \quad \Phi(u, v) := c_1 \mathcal{H}^{N-1}(Su) + \int_{\partial \Omega} |H(Tu) - H(v)| d\mathcal{H}^{N-1} + c_2 \mathcal{H}^{N-2}(Sv)$$

where H denotes a primitive of $2\sqrt{W_1}$.

The limit of F_ε in the sense of Γ -convergence in $L^1(\Omega)$ reads as

$$(1.7) \quad F(u) := \inf_v \Phi(u, v)$$

In proposition (2.3) we show that this limit F is nothing else but the relaxed functional associated with the functional F_0 as defined in (1.4). In that sense the model of capillarity with line tension is mathematically justified as the singular limit of Cahn and Hilliard model (1.3).

The consequences of this new model for equilibrium and contact angle are discussed in section 3 where examples are considered. A complete version of the results presented in section 2 will appear in a forthcoming paper [2].

2. – The convergence result

In the following Ω denotes a bounded open subset of \mathbb{R}^N with boundary of class C^2 , W_1 and W_2 are non-negative continuous functions on \mathbb{R} such that $\lim_{t \rightarrow \infty} (W_i(t)/|t|) = +\infty$ and $W_i(t) = 0 \Leftrightarrow t \in \{\alpha_i, \beta_i\}$ (with $\alpha_i < \beta_i$) for $i = 1, 2$ and H denotes a function on \mathbb{R} such that $H' = 2\sqrt{W_1}$. Finally, λ_ε is a parameter tending to infinity with a suitable scale while ε decreases to 0.

We consider the following functional on the space $L^1(\Omega)$:

$$(2.1) \quad F_\varepsilon(u) := \begin{cases} \varepsilon \int_\Omega |Du|^2 + \frac{1}{\varepsilon} \int_\Omega W_1(u) + \lambda_\varepsilon \int_{\partial \Omega} W_2(Tu) & \text{if } u \in H^1(\Omega), \\ +\infty & \text{otherwise.} \end{cases}$$

To describe the limit of F_ε , we need to introduce spaces of functions with bounded variations: if A is an open subset of \mathbb{R}^h or of some h -dimensional smooth embedded manifold, $BV(A)$ denotes the space of all real functions in $L^1(A)$ (the measure on A being the h -dimensional-Hausdorff measure), whose distributional derivatives are bounded Borel measures on A . When $u \in BV(A)$ and A is an open subset of \mathbb{R}^h , the measure Du takes values in \mathbb{R}^h , and when A is a subset of a smooth manifold M embedded in \mathbb{R}^k , then Du takes values in \mathbb{R}^k and the density of Du with respect to the total variation $|Du|$ takes values in the tangent space of M in x for $|Du|$ almost all x . The jump set Su of a function $u \in BV(A)$ (i.e. the set of all points where u has no approximate limit with respect to the h -dimensional Hausdorff measure on A) is \mathcal{H}^{h-1} -countably rectifiable. If $u \in BV(A)$ is the characteristic function 1_E of some Borel subset E , we will say that E has finite perimeter in A . In that case S_u coincides with the essential boundary of E denoted $\partial E \cap A$ and we have: $\int_A |D1_E| = \mathcal{H}^{h-1}(\partial E \cap A)$. When A has Lipschitz boundary and u belongs to $H^1(A)$ (or $BV(A)$), we denote by Tu the trace of u on A . When $u = 1_E$, this trace is the characteristic function of some Borel subset of ∂A we shall denote $E \cap \partial A$. For further properties of BV spaces, we refer to [6] [8].

The asymptotic behaviour of the functionals $F_\varepsilon(u)$ as $\varepsilon \rightarrow 0$ is described by a functional Φ which depends on two variables u and v . The variable u (volume

density) ranging into $\{\alpha_1, \beta_1\}$ is related to the limit of minimizers u_ε of (1.1) in $L^1(\Omega)$. The variable v (surface density) ranging into $\{\alpha_2, \beta_2\}$ corresponds to the limit of Tu_ε the trace of u_ε in $L^1(\partial\Omega)$. Since this limit v differs from the trace Tu , a boundary layer appears contributing to the global energy by a equivalent surface density on $\partial\Omega$ equal to $|H(Tu) - H(v)|$. The interface energy in Ω concentrated on the surface separating the volume phases $A_1 := \{u = \alpha_1\}$ and $B_1 := \{u = \beta_1\}$ is described as in [9] by the capillarity coefficient c_1 defined by:

$$(2.2) \quad c_1 := |H(\beta_1) - H(\alpha_1)| = 2 \int_{\alpha_1}^{\beta_1} \sqrt{W_1(s)} ds$$

The main feature of our model is that a minimal interface criterium appears between the surface phases $A_2 := \{v = \alpha_2\}$ and $B_2 := \{v = \beta_2\}$ represented by a line tension coefficient c_2 which depends on our scaling :

$$(2.3) \quad c_2 := (\beta_2 - \alpha_2)^2 \frac{K}{\pi}, \quad K := \lim_{\varepsilon \rightarrow 0} \varepsilon \log \lambda_\varepsilon$$

The limit energy Φ reads as:

$$(2.4) \quad \Phi(u, v) := \begin{cases} c_1 \mathcal{H}^{N-1}(Su) + \int_{\partial\Omega} |H(Tu) - H(v)| + c_2 \mathcal{H}^{N-2}(Sv) & \text{if } u \in BV(\Omega, \{\alpha_1, \beta_1\}), v \in BV(\partial\Omega, \{\alpha_2, \beta_2\}) \\ +\infty & \text{otherwise.} \end{cases}$$

We have:

THEOREM 2.1. (i) *Let (u_ε) be a sequence such that $F_\varepsilon(u_\varepsilon)$ is bounded. Then $(u_\varepsilon, T(u_\varepsilon))$ is strongly relatively compact in $L^1(\Omega) \times L^1(\partial\Omega)$. Moreover, for every cluster point (u, v) , the following lower bound inequality holds:*

$$\liminf F_\varepsilon(u_\varepsilon) \geq \Phi(u, v).$$

(ii) *Conversely, for every (u, v) in $L^1(\Omega) \times L^1(\partial\Omega)$, there exists an approximating sequence (u_ε) in $L^1(\Omega)$ such that*

$$u_\varepsilon \rightarrow u \text{ in } L^1(\Omega), \quad T(u_\varepsilon) \rightarrow v \text{ in } L^1(\partial\Omega), \quad \limsup_{\varepsilon \rightarrow 0} F_\varepsilon(u_\varepsilon) \leq \Phi(u, v)$$

REMARK. In (ii) we can choose u_ε so that $\int_\Omega u_\varepsilon dx = \int_\Omega u dx$ for every ε . This way we can fit with a prescribed total mass constraint.

We may easily reformulate the theorem 2.1 after elimination of the variable v . Setting

$$(2.5) \quad F(u) := \inf\{\Phi(u, v) : v \in L^1(\partial\Omega)\}$$

and, using the remark above, we have:

COROLLARY 2.2. *The sequence F_ε Γ -converges to F in $L^1(\Omega)$. Therefore if m satisfies $\alpha_1 < m/|\Omega| < \beta_1$ and u_ε is a minimizer for the problem:*

$$(2.6) \quad \inf\{F_\varepsilon(v) : \int_\Omega v dx = m\}$$

Then (u_ε) is strongly relatively compact in $L^1(\Omega)$ (as the trace Tu_ε in $L^1(\partial\Omega)$) by the assertion (i) of theorem 2.1) and every cluster point u is solution of

$$(2.7) \quad \inf\{F(v) : \int_\Omega v dx = m\}$$

Note that the functional $F(u)$ defined by (2.5) is non local with respect to u in the sense that it cannot be expressed by integration of a local density depending on the variables u and Du .

From a mechanical point of view, line tension is usually understood as a concentration of a part of the total energy on the contact line $\mathcal{C} := Su \cap \partial\Omega$ proportionally to its length. Of course this has sense only if \mathcal{C} (that is the jump set of the trace Tu) is \mathcal{H}^{N-2} -rectifiable. In that case the expected energy should take the form (1.4).

To recover this form in our limit model, we must assume that \mathcal{C} coincides with $S_v (= \partial A_2)$ i.e. that the infimum of $\Phi(u, \cdot)$ defined by (2.4) is achieved for $v = \alpha_2$ on A_1 (and β_2 on B_1) or for $v = \beta_2$ on A_1 (and α_2 on B_1). An easy computation shows that the second configuration cannot be optimal among the other possible choices for v corresponding to $A_2 = A_1 \cap \partial\Omega$, $A_2 = \emptyset$ or $A_2 = \partial\Omega$. So we define

$$p(\alpha_1) := \alpha_2, \quad p(\beta_1) := \beta_2$$

and

$$(2.8) \quad F_0(u) := \begin{cases} \Phi(u, p(Tu)) & \text{if } u \in BV(\Omega, \{\alpha_1, \beta_1\}), Tu \in BV(\partial\Omega) \\ +\infty & \text{otherwise} \end{cases}$$

This new functional can be expressed in term of the subset A_1 . For admissible u , A_1 has finite perimeter in Ω and its trace on $\partial\Omega$ has bounded perimeter in $\partial\Omega$ considered as a $(N-1)$ -dimensional manifold. Hence this set $\partial\Omega \cap A_1$ has a $(N-2)$ -rectifiable reduced boundary (denoted $\partial A_1 \cap \partial\Omega$) corresponding to the geometrical contact line. We have:

$$(2.9) \quad F_0(u) = c_1 \mathcal{H}^{N-1}(\partial A_1 \cap \Omega) + \hat{c}_1 \mathcal{H}^{N-1}(\partial\Omega \cap A_1) + c_2 \mathcal{H}^{N-2}(\partial A_1 \cap \partial\Omega) + d$$

where

$$(2.10) \quad \begin{aligned} \hat{c}_1 &:= |H(\alpha_2) - H(\alpha_1)| - |H(\beta_2) - H(\beta_1)| \\ d &:= |H(\beta_2) - H(\beta_1)| \mathcal{H}^{N-1}(\partial\Omega) \end{aligned}$$

A capillarity problem with line tension is associated :

$$(2.11) \quad \inf\{F_0(v) : \int_{\Omega} v dx = m\}$$

The following proposition makes the connection between F_0 and the functional F defined in (2.4):

PROPOSITION 2.3. *Assume that the following inequalities hold :*

$$(2.12) \quad \alpha_2 \leq \alpha_1 < \beta_1 \leq \beta_2$$

Then F is the relaxation of F_0 with respect to the strong topology of $L^1(\Omega)$: for every u in $L^1(\Omega)$

$$F(u) = \inf\{\liminf_{n \rightarrow \infty} F_0(u_n) : u_n \rightarrow u \text{ in } L^1\}$$

Therefore the problems (2.6) and (2.11) have the same infimum and every minimizer for (2.11) (if it exists) is also a minimizer for (2.6).

PROOF. By (2.2) and (2.12), the following equality holds for every s and t in $\{\alpha_1, \beta_1\}$:

$$(2.13) \quad |H(p(s)) - H(t)| = |H(p(s)) - H(s)| + c_1 1_{\{s \neq t\}}.$$

The inequality $F \leq F_0$ is trivial. To prove the opposite inequality, we need to prove that for every $u \in BV(\Omega, \{\alpha_1, \beta_1\})$, $v \in BV(\partial\Omega, \{\alpha_2, \beta_2\})$, we can find an approximating sequence (u_n) such that:

$$(2.14) \quad (u_n, Tu_n) \rightarrow (u, v) \text{ in } L^1(\Omega) \times L^1(\partial\Omega), \quad \limsup_{n \rightarrow \infty} F_0(u_n) \leq \Phi(u, v).$$

To that aim, we need an approximation lemma.

LEMMA. *Let A a subset of Ω with finite perimeter, $\partial A \cap \Omega$ its reduced boundary, θ a function in $L^1(\partial\Omega; \{0, 1\})$. Then there exists a sequence of sets (A_n) with finite perimeter in Ω such that $|A_n \Delta A| \rightarrow 0$ and*

$$(2.15) \quad \mathcal{H}^{N-1}(\partial A_n \cap \Omega) \rightarrow \mathcal{H}^{N-1}(\partial A \cap \Omega) + H^{N-1}(\{T(1_A \neq \theta)\})$$

For given (u, v) , we use the sequence (A_n) defined by this lemma with $A := \{u = \alpha_1\}$ and $\theta := 1_{\{v = \alpha_2\}}$. Then (2.14) is obtained by taking $u_n := \alpha_1 1_{A_n} + \beta_1 1_{\Omega - A_n}$. Indeed we have $p(Tu_n) = v$ and applying (2.13) with $(s, t) = (p^{-1}(v), v)$, by (2.15), one gets:

$$\begin{aligned} \limsup_{n \rightarrow \infty} F_0(u_n) &\leq \limsup_{n \rightarrow \infty} (c_1 \mathcal{H}^{N-1}(\partial A_n \cap \Omega) + c_2 \mathcal{H}^{N-2}(S_v) + \\ &\quad + \int_{\partial\Omega} |H(v) - H(p^{-1}(v))| d\mathcal{H}^{N-1}) \\ &\leq c_1 \mathcal{H}^{N-1}(\partial A \cap \Omega) + c_2 \mathcal{H}^{N-2}(S_v) + \\ &\quad + \int_{\partial\Omega} (|H(v) - H(p^{-1}(v))| + c_1 1_{\{p^{-1}(v) \neq Tu\}}) d\mathcal{H}^{N-1} \\ &\leq c_1 \mathcal{H}^{N-1}(\partial A \cap \Omega) + c_2 \mathcal{H}^{N-2}(S_v) + \\ &\quad + \int_{\partial\Omega} (|H(v) - H(Tu)|) d\mathcal{H}^{N-1} = \Phi(u, v). \quad \square \end{aligned}$$

PROOF OF THE LEMMA

As well known [8] there exists an approximating sequence (u_n) in $BV(\Omega)$ such that $u_n \rightarrow 1_A$, $T(u_n) = \theta$ and

$$(2.16) \quad \int_{\Omega} |Du_n| \rightarrow \int_{\Omega} |D1_A| + \int_{\partial\Omega} |\theta - 1_A| d\mathcal{H}^{N-1}$$

Moreover, by using truncation, we can assume that: $|u_n| \leq 1$. For every $t \in]0, 1[$ let us consider the level set $\{u_n > t\}$. As $\theta \in \{0, 1\}$ the Lebesgue density (with respect to Ω) of this set at a point of $\partial\Omega$ is \mathcal{H}^{N-1} a.e. equal to 1 on $\{\theta = 1\}$ and to 0 on $\{\theta = 0\}$ so its trace on $\partial\Omega$ coincides with θ . Now by the coarea-formula $\int_{\Omega} |Du_n| = \int_0^1 (\int_{\Omega} |D1_{\{u_n > t\}}|) dt$ we see that, for every $\delta > 0$, there exists $t_n \in [\delta, 1 - \delta]$ such that:

$$(2.17) \quad \int_{\Omega} |D1_{\{u_n > t_n\}}| \leq \frac{1}{1 - 2\delta} \left(\int_{\Omega} |Du_n| \right)$$

Then the sequence $A_n := \{u_n > t_n\}$ satisfies the conditions of lemma. Indeed as seen above $T(1_{A_n}) = \theta$ and by (2.16) and (2.17):

$$\limsup_{n \rightarrow \infty} \int_{\Omega} |D1_{A_n}| \leq \frac{1}{1 - 2\delta} \left(\int_{\Omega} |Du| + \int_{\partial\Omega} |\theta - 1_A| d\mathcal{H}^{N-1} \right)$$

which yields (2.15) by letting δ tend to 0. Moreover, due to the identity $\int_{\Omega} |u_n - 1_A| dx = \int_0^1 (\int_{\Omega} |1_{\{u_n > t\}} - 1_A| dx) dt$ we deduce from the convergence of u_n to 1_A in $L^1(\Omega)$ that a subsequence of $f_n(t) := \int_{\Omega} (1_{\{u_n > t\}} - 1_A)^+ dx$ converges to 0 a.e., hence uniformly on $[\delta, 1 - \delta]$ since f_n is non increasing with respect to t . The same conclusion holds for $g_n(t) := \int_{\Omega} (1_{\{u_n > t\}} - 1_A)^- dx$ (which is non decreasing with respect to t). The convergence of $|A_n \Delta A| = f_n(t_n) + g_n(t_n)$ to 0 follows and the lemma is proved. \square

OUTLINE OF THE PROOF OF THEOREM 2.1

For all details we refer to [2]. The main point in the proof of (i) is the strong relative compactness of the traces (Tu_ε) in $L^1(\partial\Omega)$. To that aim, we consider a neighborhood A of the boundary and the localized part of the total associated energy, say $F_\varepsilon(u, A)$. Up to a diffeomorphism, we can assume that $A = \{x \in \mathbb{R}^N : |x| < r, x_N > 0\}$. By a slicing argument we reduce to the case $N = 2$. Then we show that $F_\varepsilon(u, A)$ is lower bounded by $G_\varepsilon(Tu_\varepsilon)$ where G_ε is the following 1-dimensional energy:

$$G_\varepsilon(v) := \frac{\varepsilon}{2\pi} \iint_{]-r, r[^2} \left| \frac{v(x') - v(x)}{x' - x} \right|^2 dx' dx + \lambda_\varepsilon \int_{]-r, r[} W_2(v) dx$$

Finally we apply to G_ε the compactness and the Γ -convergence result we proved in [1] (which provides in particular the strong relative compactness in $L^1(A \cap \partial\Omega)$ of (Tu_ε)).

Let us now outline the proof of the assertion (ii). By a standard approximation procedure for sets of finite perimeter, we reduce to the case where the boundary phases A_1 and B_1 are separated by a smooth curve \mathcal{L} . Far from \mathcal{L} , we use the same approximating sequence (u_ε) as in [9]. On a neighborhood of \mathcal{L} (a rectangular cylinder Q_ε as displayed in Fig. 1 where the level sets of u_ε are drawn) we use the cylindrical coordinates (r, θ) .

Defining $r_\varepsilon := \frac{\varepsilon}{\log \lambda_\varepsilon}$ and $R_\varepsilon := +\frac{\varepsilon}{2}$, we choose for (u_ε) a function which is continuous across ∂Q_ε , affine and depending only on θ in the crown $\{r_\varepsilon < r < R_\varepsilon\}$ and such that:

$$\begin{aligned} Tu_\varepsilon &= \beta_2 \text{ if } r \geq r_\varepsilon \text{ and } \theta = 0 \quad ; \quad Tu_\varepsilon = \alpha_2 \text{ if } r \geq r_\varepsilon \text{ and } \theta = \pi \\ |Du_\varepsilon| &\leq \frac{M}{\varepsilon} \text{ if } r \geq R_\varepsilon \quad ; \quad |Du_\varepsilon| \leq \frac{M}{r_\varepsilon} \text{ if } r \leq r_\varepsilon \end{aligned}$$

The total energy on Q_ε corresponding to u_ε is upper bounded:

$$F_\varepsilon(u_\varepsilon, Q_\varepsilon) \leq \mathcal{H}^{N-2}(\mathcal{L}) \left[\varepsilon \frac{|\beta_2 - \alpha_2|^2}{\pi} \int_{r_\varepsilon}^{R_\varepsilon} \frac{dr}{r} + 2\lambda_\varepsilon r_\varepsilon \sup_{[\alpha_2, \beta_2]} W_2 + o(\varepsilon) \right]$$

so that the limit of this contribution as ε tends to 0 is upper bounded by $\widehat{c}_2 \mathcal{H}^{N-2}(\mathcal{L})$.

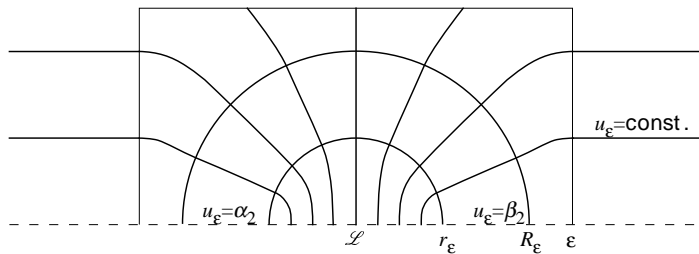


FIGURE 1

3. – Capillary equilibrium with line tension

In this section we give some examples of equilibrium, i.e. minimizers (u, v) of the functional Φ defined in (2.4). In particular we show how for some particular geometries of the container, the dissociation between the contact line and the surface phase transition is possible. Let us consider two phases $A_1 := \{u = \alpha_1\}$ and $B_1 := \{u = \beta_1\}$ in equilibrium in a container Ω as partially drawn in Fig. 2. The trace of the interface S is the curve \mathcal{C} (contact line). We assume that two boundary

phases $A_2 := \{v = \alpha_2\}$ and $B_2 := \{v = \beta_2\}$ lie on $\partial\Omega$ and are separated by the curve \mathcal{L} .

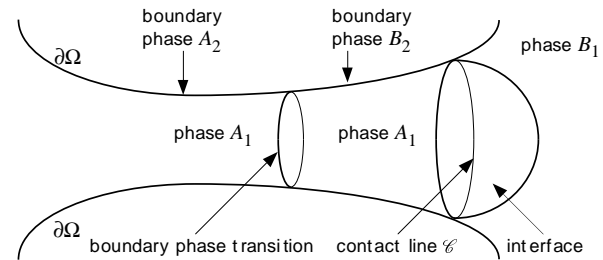


FIGURE 2

Assuming everything smooth, we define φ on the curve \mathcal{L} as the angle between the inward normal n to $\partial\Omega$ and the principal normal to \mathcal{L} and \mathcal{K} as the curvature of \mathcal{L} . We define θ on \mathcal{C} as the angle between the interface and the boundary (the contact angle – see Fig. 3). Let us write the conditions of equilibrium corresponding to a stationary point for $\Phi(u, v)$. When \mathcal{L} and \mathcal{C} do not coincide these conditions read as:

$$(3.1) \quad |H(\alpha_1) - H(\alpha_2)| - |H(\alpha_1) - H(\beta_2)| + c_2 \mathcal{K} \sin \varphi = 0 \quad \text{on } \mathcal{L},$$

$$(3.2) \quad |H(\beta_1) - H(\beta_2)| - |H(\alpha_1) - H(\beta_2)| + c_1 \cos \theta = 0 \quad \text{on } \mathcal{C}.$$

These optimality conditions may be interpreted in term of forces as shown in Fig. 3.

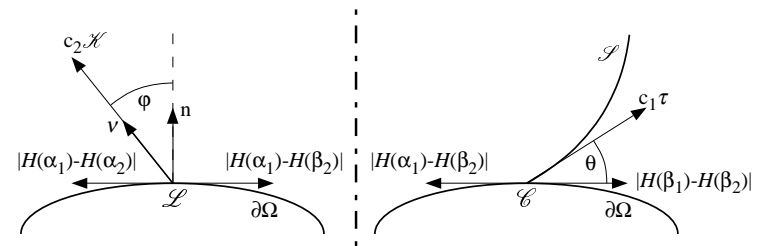


FIGURE 3

Equation (3.2) fixes the value of the contact angle. Then for a prescribed volume of the phase A_1 , the position of the interface is given. Equation (3.1) fixes the position of the curve \mathcal{L} through the purely geometrical quantities \mathcal{K} and φ . When \mathcal{C} and \mathcal{L} are disconnected the position of \mathcal{L} does not depend on the position of the interface.

When \mathcal{C} and \mathcal{L} coincide the equilibrium conditions read as:

$$(3.3) \quad |H(\alpha_1) - H(\alpha_2)| - |H(\beta_1) - H(\beta_2)| + c_2 \mathcal{K} \sin \varphi + c_1 \cos \theta = 0$$

$$(3.4) \quad \begin{aligned} - |H(\alpha_1) - H(\alpha_2)| + |H(\alpha_1) - H(\beta_2)| &\leq \\ &\leq c_2 \mathcal{K} \sin \varphi \leq |H(\beta_1) - H(\beta_2)| - |H(\beta_1) - H(\alpha_2)| \end{aligned}$$

EXAMPLE: A BUBBLE GROWING IN A CYLINDER

Let us consider a bubble of volume V in a cylinder Ω of radius R . V is sufficient for the bubble to reach the boundary ($V \geq \frac{4\pi}{3}R^3$) (see Fig. 4).

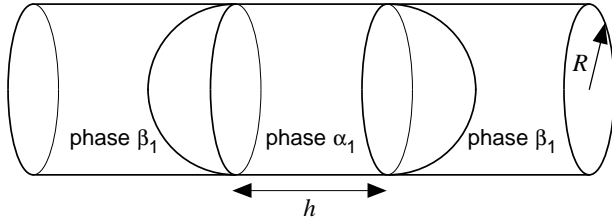


FIGURE 4

Two situations have to be considered: 1) There is a unique boundary phase $\{v = \beta_2\}$; 2) The boundary phases coincide with the volume phases ($v = p(Tu)$).

In the first case the contact angle is:

$$\theta_1 = \arccos \left(\frac{|H(\beta_1) - H(\beta_2)| - |H(\alpha_1) - H(\beta_2)|}{c_1} \right),$$

while in the second case the contact angle is

$$\theta_2 = \arccos \left(\frac{|H(\beta_1) - H(\beta_2)| - |H(\alpha_1) - H(\alpha_2)|}{c_1} \right).$$

(Due to the geometry of the container the line tension has no effect on this angle).

For small bubbles only the first situation is less energetic. Indeed let us compute the energies in the very simple case: $\alpha_1 = \alpha_2$ and $\beta_1 = \beta_2$. Then $\theta_1 = \pi$, $\theta_2 = \pi/2$, the energy in the first case is:

$$E_1 = \frac{2c_1}{R}V + \frac{4\pi}{3}c_1R^2$$

while in the second case it is:

$$E_2 = 4\pi R^2 c_1 + 2\pi R c_2.$$

Then the first state is less energetic for

$$V \leq V_0 := \pi R^2 \left(\frac{c_2}{c_1} + \frac{4}{3}R \right).$$

So the contact angle for such a growing bubble will jump from θ_1 to θ_2 when the volume reaches the critical value R_0 .

This example can be extended to a growing bubble on a plane boundary. The explicit computation is tedious in that case. The bubble will first grow with a constant contact angle (and a unique boundary phase) then reach a critical volume V_0 , the contact angle will suddenly change. For larger bubbles the decreasing of the effect of line tension will lead to an increasing contact angle.

These examples show that capillary equilibrium with line tension cannot be studied forgetting boundary phases and the possibility of dissociation between the support of line tension and the geometrical contact line.

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G. Alberti, Istituto di Matematiche Applicate "U. Dini", Università di Pisa, via Bonanno 25/B, 56126 Pisa, Italy.

G. Bouchitté and P. Seppecher, UFR Science, Université de Toulon et du Var, BP 132, 83957 La Garde Cedex France.