

Boundary conditions for a capillary fluid in contact with a wall

H. GOUIN (MARSEILLE) and W. KOSIŃSKI (WARSZAWA)

CONTACT OF A FLUID with a solid or an elastic wall is investigated. The wall exerts “molecular forces” on the fluid which is locally strongly non-homogeneous. The problem is approached with a fluid energy of the second gradient form and a wall surface energy depending on the value of the fluid density in the contact. From the virtual work principle and taking into account the fluid density, its derivative normal to the wall and the curvature of the surface, limit conditions are obtained.

1. Introduction

THE PHENOMENON OF SURFACE wetting is a subject of many experiments [1]. Such experiments have been used to determine many important properties of the wetting behaviour for liquid on low energy surface [2]. In fact the wetting transition of fluids in contact with solid surfaces is an important field of research both for mechanics and physical chemistry. In the recent paper [3], the first author using statistical methods has proposed an explicit form for the energy of interaction between solid surfaces and liquids. This energy yields a bridge connecting statistical mechanics and continuum mechanics. To obtain the boundary conditions between fluid and solid, it is also necessary to know the behaviour of the fluid as well as the solid.

We propose a mechanical model similar to that used in the mean-field theory of capillarity that leads to the second gradient theory of continuous media in fluid mechanics [4]. The theory is conceptually more straightforward than the Laplace one to build a model of capillarity [5, 6]. That theory takes into account systems in which fluid interfaces are present [7]. The internal capillarity is one of the simplest cases since we are able to calculate the surface tension in the case of thin interfaces as well as in thick ones [8]. It is possible to obtain the nucleation of drops and bubbles [9].

It seems that the approximation of the mean-field theory is too simple to be quantitatively accurate. However, it does provide a qualitative understanding. Moreover, the point of view, that the fluid in interfacial region may be treated as a bulk phase with a local free energy density and an additional contribution arising from the nonuniformity which may be approximated by a gradient expansion truncated at the second order terms, is most likely to be successful and perhaps even quantitatively accurate near the critical point [10].

In this paper we connect both the interaction of a solid surface and a fluid phase by means of the virtual work principle. The distribution of fluid energy in the volume and the surface density energy on the solid surface yield the boundary conditions. The conditions are different from those obtained for a classical fluid within the theory of gas dynamics. We obtain an embedding effect for the density of the fluid; moreover, the conditions take into account the curvature of the surface. The result is extended to the case of an elastic wall. A discussion is obtained depending on the value of the density of the fluid at the surface.

Let us use asterisk $*$ to denote *conjugate* (or *transpose*) mappings or covectors (line vectors). For any vectors \mathbf{a}, \mathbf{b} we shall use the notation $\mathbf{a}^* \mathbf{b}$ for their *scalar product* (the line vector is multiplied by the column vector), $\mathbf{a} \cdot \mathbf{b}$ and $\mathbf{a} \mathbf{b}^*$ for their *tensor product* (the column vector is multiplied by the line vector) $\mathbf{a} \otimes \mathbf{b}$. The product of a mapping A by a vector \mathbf{a} is denoted by $A \mathbf{a}$. Notation $\mathbf{b}^* A$ means covector \mathbf{c}^* defined by the rule $\mathbf{c}^* = (A^* \mathbf{b})^*$. The divergence of a linear transformation A is the covector $\text{div} A$ such that, for any constant vector \mathbf{a} ,

$$\text{div}(A) \mathbf{a} = \text{div}(A \mathbf{a}).$$

If $f(\mathbf{x})$ is a scalar function of the vector \mathbf{x} associated with the Euler variables in the physical space, $\partial f / \partial \mathbf{x}$ is the linear form associated with the gradient of f and consequently, $\left(\frac{\partial f}{\partial \mathbf{x}}\right)^* = \text{grad } f$.

2. Continuous mechanical model of capillary layers

We consider a fluid in contact with a solid. The fluid occupies the domain D and its boundary Σ which is common with the solid wall. Physical experiments prove that the fluid is nonhomogeneous in the neighbourhood of Σ [10]. It is also possible to consider the fluid as a continuous medium by taking into account a "capillary layer" existing in the vicinity of Σ and a form of its stress tensor [11]. One way to present the behaviour of such a fluid is to consider the specific internal energy ε as a function of the density ρ as well as $\text{grad } \rho$. Such an expression is known in continuum mechanics as *internal capillary energy*, see [4, 5]. It is related to molecular models of strongly nonhomogeneous fluids in the frame of the mean field theory and is equivalent to the van der Waals model of capillarity (see the review by ROWLINSON and WIDOM [10]). The energy ε is also a function of the specific entropy. In the case of isothermal media at a given temperature, the specific internal energy is replaced by the specific free energy. In the mechanical case, the entropy or the temperature are not concerned by the virtual variations of the medium. Consequently, for an isotropic fluid, it is assumed that

$$\varepsilon = f(\rho, \beta),$$

where $\beta = \text{grad } \rho \cdot \text{grad } \rho$. The fluid is subjected to external forces represented by a force potential Ω per unit mass as a function of Eulerian variables \mathbf{x} .

We denote by $\Sigma \ni \mathbf{x} \rightarrow B(\mathbf{x}) \in R$ the surface density of energy of the solid wall. The total energy E of the fluid in D and its boundary Σ is the sum of the three terms expressing: internal energy E_f , potential energy E_p and surface energy E_S : $E = E_f + E_p + E_S$, with

$$E_f = \int_D \rho \varepsilon(\rho, \beta) dv, \quad E_p = \int_D \rho \Omega(\mathbf{x}) dv, \quad E_S = \int_{\Sigma} B ds.$$

Let us denote by δ a variation of the position of the fluid as in [12]. The variation is associated with the *virtual displacement*

$$D \ni x \rightarrow \delta \mathbf{x} = \zeta(\mathbf{x}).$$

We have the following results presented in the Appendix,

$$(2.1) \quad \delta E_f = \int_D (-\text{div } \sigma) \cdot \zeta dv + \int_{\Sigma} \left\{ -A \frac{d\zeta_n}{dn} + \left(\frac{2A}{R_m} \mathbf{n} + \text{grad}_{tg} A + \sigma \mathbf{n} \right) \cdot \zeta \right\} ds$$

with

$$\sigma = -P\mathbf{I} - C \text{grad} \rho \otimes \text{grad} \rho = -P\mathbf{I} - C \left(\frac{\partial \rho}{\partial \mathbf{x}} \right)^* \frac{\partial \rho}{\partial \mathbf{x}},$$

where $C = 2\rho \varepsilon'_\beta$ and $P = \rho^2 \varepsilon'_\rho - \rho \text{div} (C \text{grad } \rho)$, ε'_ρ denotes the partial derivative of ε with respect to ρ , $\zeta_n = \mathbf{n}^* \zeta$ where \mathbf{n} is the external unit normal to Σ and $A = C\rho \frac{d\rho}{dn}$ where $\frac{d\rho}{dn} = \frac{\partial \rho}{\partial \mathbf{x}} \mathbf{n}$.

The scalar R_m is the mean curvature of Σ and grad_{tg} is the tangential part of grad relatively to Σ .

Moreover,

$$(2.2) \quad \delta E_p = \int_D \rho \frac{\partial \Omega}{\partial \mathbf{x}} \zeta dv = \int_D \rho \text{grad } \Omega \cdot \zeta dv,$$

and using the results presented in the Appendix,

$$(2.3) \quad \delta E_S = \int_{\Sigma} \left(\delta B - \left(\frac{2B}{R_m} \mathbf{n} + \text{grad}_{tg} B \right) \cdot \zeta \right) ds.$$

One assumes that the volumetric mass in the fluid has a limit, interfacial value ρ_s at the wall Σ (which is not the surface density of the wall but the mass

density per unit volume as in the shock wave analysis). One assumes also that B is a function of ρ_s only. These hypotheses are confirmed by results presented in [3]. Then,

$$\delta B = B'(\rho_s)\delta\rho_s = -\rho_s B'(\rho_s) \operatorname{div} \zeta.$$

Let us denote $G = -\rho_s B'_{\rho_s}$. Consequently,

$$\int_{\Sigma} \delta B \, ds = \int_{\Sigma} G \operatorname{div} \zeta \, ds = \int_{\Sigma} \left(G \frac{d\zeta_n}{dn} - \frac{2G}{R_m} \mathbf{n} \cdot \zeta - \operatorname{grad}_{tg} G \cdot \zeta \right) ds$$

(see Appendix).

Now, $H = B(\rho_s) - \rho_s B'_{\rho_s}(\rho_s)$ is the Legendre transformation of B with respect to ρ_s . Then,

$$(2.4) \quad \delta E_S = \int_{\Sigma} \left(G \frac{d\zeta_n}{dn} - \left(2H \frac{\mathbf{n}}{R_m} + \operatorname{grad}_{tg} H \right) \cdot \zeta \right) ds.$$

The d'Alembert-Lagrange *principle of virtual works* is expressed in the form [12]:

$$(2.5) \quad \forall D \ni \mathbf{x} \rightarrow \zeta(\mathbf{x}), \quad \delta E = 0.$$

Consequently, from the fundamental lemma of variation calculus, we obtain the balance equation in the fluid D and the boundary conditions on the solid wall Σ .

Equilibrium equations

From any arbitrary variation $D \ni \mathbf{x} \rightarrow \zeta(\mathbf{x})$ such that $\zeta = 0$ on Σ , we take first

$$\int_D \left(\rho \frac{\partial \Omega}{\partial \mathbf{x}} - \operatorname{div} \sigma \right) \cdot \zeta \, dv = 0.$$

Consequently,

$$(2.6) \quad \operatorname{div} \sigma - \rho \frac{\partial \Omega}{\partial \mathbf{x}} = 0.$$

This equation is the well known equilibrium equations [5, 7, 9]

Boundary conditions

a) Case of a rigid (undeformed) wall.

We consider a rigid wall. Consequently, the virtual displacements satisfy on Σ the condition $\mathbf{n}^* \zeta = 0$. Then,

$$\int_{\Sigma} \left\{ (G - A) \frac{d\zeta_n}{dn} + \left(\frac{2(A - H)}{R_m} \mathbf{n} + \operatorname{grad}_{tg}(A - H) + \sigma \mathbf{n} \right) \cdot \zeta \right\} ds = 0$$

at the rigid wall.

Hence, we deduce the boundary conditions at the rigid wall:

$$(2.7) \quad \text{for } \mathbf{x} \in \Sigma : \quad G - A = 0$$

and moreover, there exists a Lagrange multiplier $\Sigma \ni \mathbf{x} \rightarrow \lambda(\mathbf{x}) \in \mathbb{R}$ such that

$$(2.8) \quad \frac{2(A - H)}{R_m} \mathbf{n} + \text{grad}_{tg}(A - H) + \sigma \mathbf{n} = \lambda \mathbf{n}.$$

b) Case of an elastic (non-rigid) solid wall.

In such a case the equilibrium equation (2.6) is unchanged. On Σ , moreover, the condition (2.7) is also unchanged. The only different condition comes from the fact that we do not have anymore the slipping condition for the virtual displacement ($\mathbf{n}^* \boldsymbol{\zeta} = 0$).

Due to the possible deformation of the wall, the virtual work of mechanical stresses on Σ is,

$$\delta E_e = \int_{\Sigma} \mathbf{t}^* \boldsymbol{\zeta} \, ds$$

with $\mathbf{t} = \mathbf{T} \mathbf{n}$ representing the stress (loading) vector, where \mathbf{T} is the value of the Cauchy stress tensor of the elastic wall on the boundary Σ . Relation (2.8) is replaced by:

$$(2.9) \quad 2 \frac{(A - H)}{R_m} \mathbf{n} + \text{grad}_{tg}(A - H) + \sigma \mathbf{n} = -\mathbf{t}.$$

3. Analysis of the boundary conditions

Relation (2.7) yields:

$$(3.1) \quad C \frac{d\rho}{dn} + B'_{\rho_s} = 0$$

and we obtain

$$H - A = B.$$

Consequently, from the definition of σ ,

$$\sigma \mathbf{n} = P \mathbf{n} - C \frac{d\rho}{dn} \text{grad} \rho.$$

Then the tangential part of equation (2.8) is always verified and equation (2.8) yields the value of the Lagrange multiplier λ .

For an elastic (non-rigid) solid wall we obtain

$$(3.2) \quad t_{tg}^* = 0 \quad \text{and} \quad t_n = \frac{2B}{R_m} + P - B'_{\rho_s} \frac{d\rho}{dn},$$

where t_{tg}^* and t_n are the tangential and the normal components of \mathbf{t} , respectively. Taking into account (3.1), $t_n = P + \frac{2B}{R_m} + \frac{1}{C}(B'_{\rho_s})^2$ and equations (3.2) yield the value of the stresses in the elastic (nonrigid) medium. The only new condition comes from (3.1).

We have the next consequences. In [3] it is proposed the surface energy in the form $B(\rho_s) = -\gamma_1\rho_s + \frac{\gamma_2}{2}\rho_s^2$, with γ_1 , and γ_2 as two positive constants. We obtain the condition for the fluid density on the wall

$$(3.3) \quad C \frac{d\rho}{dn} = \gamma_1 - \gamma_2\rho_s,$$

and hence $\frac{d\rho}{dn}$ is positive (or negative) in the vicinity of the wall if $\rho_s < \rho_i$ (or $\rho_s \geq \rho_i$) with $\rho_i = \gamma_1/\gamma_2$ which is the *bifurcation fluid density* at the wall.

If $\rho_s < \rho_i$, we have a lack of fluid density at the wall. If $\rho_s \geq \rho_i$, we have an excess of fluid density at the wall.

4. Conclusion

For a conservative medium, the first gradient theory corresponds to the case of compressibility. To take into account the superficial effects acting between solids and fluids, we propose to use the model of fluids endowed with capillarity. The theory interpretes the capillarity in a continuous way and contains Laplace's theory. The model corresponds for solids to "elastic materials with couple stresses" indicated by TOUPIN in [13].

We notice that the extension to the dynamic case is straightforward: by the virtual work principle, equation (2.6) takes the form:

$$\rho\gamma - \operatorname{div}\sigma + \rho \frac{\partial\Omega}{\partial\mathbf{x}} = 0,$$

where γ denotes the acceleration of the fluid. Equations (3.1)–(3.3) and consequences in Sec. 3 are unchanged.

Appendix

First of all, we recall the following fact from the differential geometry: Let Σ be a surface in the 3-dimensional space and \mathbf{n} its external normal.

For any vector field ζ ,

$$\mathbf{n}^* \operatorname{rot}(\mathbf{n} \times \zeta) = \operatorname{div} \zeta + \frac{2}{R_m} \mathbf{n}^* \zeta - \mathbf{n}^* \frac{\partial\zeta}{\partial\mathbf{x}} \mathbf{n}.$$

Then, for any scalar field A , we obtain :

$$\begin{aligned}
 \text{(A.1)} \quad A \operatorname{div} \zeta &= A \frac{d\zeta_n}{dn} - \frac{2A}{R_m} \zeta_n - (\operatorname{grad}_{lg}^* A) \zeta + \mathbf{n}^* \operatorname{rot} (A\mathbf{n} \times \zeta) \\
 &= \operatorname{tr} \left[\left(\frac{\partial A}{\partial \mathbf{x}} (\mathbf{nn}^* - \mathbf{1}) - \frac{2A}{R_m} \mathbf{n}^* \right) \zeta \right] + A \frac{d\zeta_n}{dn} + \mathbf{n}^* \operatorname{rot} (A\mathbf{n} \times \zeta).
 \end{aligned}$$

Let us calculate δE_f : since D is a material volume,

$$E_f = \int_D \rho \varepsilon \, dv \Rightarrow \delta E_f = \int_D \rho \delta \varepsilon \, dv$$

with $\delta \varepsilon = \frac{\partial \varepsilon}{\partial \rho} \delta \rho + \frac{\partial \varepsilon}{\partial \beta} \delta \beta$. From $\delta \frac{\partial \rho}{\partial \mathbf{x}} = \frac{\partial \delta \rho}{\partial \mathbf{x}} - \frac{\partial \rho}{\partial \mathbf{x}} \frac{\partial \zeta}{\partial \mathbf{x}}$, we deduce:

$$\rho \varepsilon'_\beta \delta \beta = 2\rho \varepsilon'_\beta \delta \left(\frac{\partial \rho}{\partial \mathbf{x}} \right) \frac{\partial \rho^*}{\partial \mathbf{x}} = C \left(\left(\frac{\partial \delta \rho}{\partial \mathbf{x}} - \frac{\partial \rho}{\partial \mathbf{x}} \frac{\partial \zeta}{\partial \mathbf{x}} \right) \right) \frac{\partial \rho^*}{\partial \mathbf{x}}$$

with $2\rho \varepsilon'_\beta = C$.

In the mean-field molecular theory, the quantity C is assumed to be constant [10], but it is not necessary. One can suppose that the scalar C is a general function of ρ and even β . Then

$$\rho \varepsilon'_\beta \delta \beta = \operatorname{div} (C \operatorname{grad} \rho \delta \rho) - \operatorname{div} (C \operatorname{grad} \rho) \delta \rho - \operatorname{tr} \left(C \operatorname{grad} \rho \operatorname{grad}^* \rho \frac{\partial \zeta}{\partial \mathbf{x}} \right).$$

Due to the fact that $\delta \rho = -\rho \operatorname{div} \zeta$ (see [12]),

$$\begin{aligned}
 \rho \delta \varepsilon &= \operatorname{div} (C \operatorname{grad} \rho \delta \rho) - \left(\rho^2 \varepsilon'_\rho - \rho \operatorname{div} (C \operatorname{grad} \rho) \right) \operatorname{div} \zeta \\
 &\quad - \operatorname{div} (C \operatorname{grad} \rho \operatorname{grad}^* \rho \zeta) + \operatorname{div} (C \operatorname{grad} \rho \operatorname{grad}^* \rho) \zeta \\
 \rho \delta \varepsilon &= \operatorname{div} (C \operatorname{grad} \rho \delta \rho - (C \operatorname{grad} \rho \operatorname{grad}^* \rho) \zeta - P \zeta) \\
 &\quad + \frac{\partial P}{\partial \mathbf{x}} \zeta + \operatorname{div} (C \operatorname{grad} \rho \operatorname{grad}^* \rho) \zeta.
 \end{aligned}$$

Then

$$\begin{aligned}
 \delta E_f &= \int_D \left(\frac{\partial P}{\partial \mathbf{x}} + \operatorname{div} (C \operatorname{grad} \rho \operatorname{grad}^* \rho) \right) \zeta \, dv \\
 &\quad + \int_D \operatorname{div} (-C \rho \operatorname{grad} \rho \operatorname{div} \zeta - C \operatorname{grad} \rho \operatorname{grad}^* \rho \zeta - P \zeta) \, dv \\
 &= \int_D -(\operatorname{div} \sigma) \zeta \, dv + \int_\Sigma (-A \operatorname{div} \zeta + \mathbf{n}^* \sigma \zeta) \, ds.
 \end{aligned}$$

Taking into account (A.1), we deduce immediately

$$\delta E_f = \int_D -(\operatorname{div} \sigma) \zeta \, dv + \int_{\Sigma} \left(-A \frac{d\zeta_n}{dn} + \left(\frac{2A}{R_m} \mathbf{n}^* + \operatorname{grad}_{t_g}^* A + \mathbf{n}^* \sigma \right) \zeta \right) ds \\ + \int_{\Sigma} \mathbf{n}^* \operatorname{rot}(A \mathbf{n} \times \zeta) \, ds.$$

$$\text{But, } \int_{\Sigma} \mathbf{n}^* \operatorname{rot}(A \mathbf{n} \times \zeta) \, ds = \int_{\Gamma} A \mathbf{t} \cdot (\mathbf{n} \times \zeta) \, dl = \int_{\Gamma} A(\mathbf{t}, \mathbf{n}, \zeta) \, dl,$$

where Γ is the line boundary of Σ and \mathbf{t} its tangent unit vector. If $\mathbf{n}' = \mathbf{t} \times \mathbf{n}$, we obtain the relation

$$(A.2) \quad \delta E_f = \int_D (-\operatorname{div} \sigma) \zeta \, dv + \int_{\Sigma} \left(-A \frac{d\zeta_n}{dn} + \left(\frac{2A}{R_m} \mathbf{n}^* + \operatorname{grad}_{t_g}^* A + \mathbf{n}^* \sigma \right) \zeta \right) ds + \int_{\Gamma} A \mathbf{n}'^* \zeta \sigma \, dl.$$

In the following, we assume that Σ has no boundary and consequently, the term associated with Γ vanishes.

Let us calculate δE_S

$$E_S = \int_{\Sigma} B \, ds.$$

Then

$$(A.3) \quad \delta E_S = \int_{\Sigma} \left\{ \delta B - \left(\mathbf{n}^* \frac{2B}{R_m} + \operatorname{grad}^* B (1 - \mathbf{nn}^*) \right) \zeta \right\} ds + \int_{\Gamma} A \mathbf{n}'^* \zeta \, dl.$$

We notice that $\operatorname{grad}^* B (1 - \mathbf{nn}^*)$ belongs to the tangent plane to Σ .

Let us prove Eq. (A.3). If we write $E_S = \int_{\Sigma} B \det(\mathbf{n}, d_1 \mathbf{x}, d_2 \mathbf{x})$ where $d_1 \mathbf{x}$ and $d_2 \mathbf{x}$ are the coordinate lines of Σ , we may write

$$E_S = \int_{\Sigma_0} B \det F \det (F^{-1} \mathbf{n}, d_1 \mathbf{X}, d_2 \mathbf{X}),$$

where Σ_0 is the image of Σ in a reference space in Lagrangian coordinates \mathbf{X} , and F is the deformation gradient tensor $\partial \mathbf{x} / \partial \mathbf{X}$.

Then,

$$\delta E_S = \int_{\Sigma_0} \delta B \det F \det (F^{-1} \mathbf{n}, d_1 \mathbf{X}, d_2 \mathbf{X}) + \int_{\Sigma_0} B \delta \left(\det F \det (F^{-1} \mathbf{n}, d_1 \mathbf{X}, d_2 \mathbf{X}) \right).$$

Moreover,

$$\begin{aligned} \int_{\Sigma_0} B \delta \left(\det F \det (F^{-1} \mathbf{n}, d_1 \mathbf{X}, d_2 \mathbf{X}) \right) &= \int_{\Sigma} B \operatorname{div} \zeta \det (\mathbf{n}, d_1 \mathbf{x}, d_2 \mathbf{x}) \\ &+ B \det \left(\frac{\partial \mathbf{n}}{\partial \mathbf{x}} \zeta, d_1 \mathbf{x}, d_2 \mathbf{x} \right) - B \det \left(\frac{\partial \zeta}{\partial \mathbf{x}} \mathbf{n}, d_1 \mathbf{x}, d_2 \mathbf{x} \right) \\ &= \int_{\Sigma} \left(\operatorname{div}(B \zeta) - \operatorname{grad}^* B \zeta - B \mathbf{n}^* \frac{\partial \zeta}{\partial \mathbf{x}} \mathbf{n} \right) ds. \end{aligned}$$

From (A.1) we obtain

$$\operatorname{div}(B \zeta) - B (\operatorname{div} \mathbf{n}) \mathbf{n}^* \zeta - \mathbf{n}^* \frac{\partial B \zeta}{\partial \mathbf{x}} \mathbf{n} = \mathbf{n}^* \operatorname{rot} (B \mathbf{n} \times \zeta).$$

Then,

$$\begin{aligned} \int_{\Sigma_0} B \delta \left(\det F \det (F^{-1} \mathbf{n}, d_1 \mathbf{X}, d_2 \mathbf{X}) \right) &= \int_{\Sigma_0} (B (\operatorname{div} \mathbf{n}) \mathbf{n}^* \\ &+ \operatorname{grad}^* B (\mathbf{n} \mathbf{n}^* - \mathbf{1})) \zeta ds + \int_{\Sigma} \mathbf{n}^* \operatorname{rot} (B \mathbf{n} \times \zeta) ds \end{aligned}$$

and we obtain (A.3) with $\operatorname{div} \mathbf{n} = -\frac{2}{R_{cm}}$.

We assume that Σ has no boundary and consequently, the term associated with Γ is null.

Acknowledgment

The authors are grateful to the Polonium Program of Co-operation No. 7075 between the Polish Committee for Scientific Research (KBN) and French Foreign Office for the financial support of this research.

References

1. A. E. VAN GIESSEN, D. J. BUKMAN, B. WIDOM, *Contact angles of liquid drops on low-energy solid surfaces*, J. Colloid Interface Sci., **192**, 257–265, 1997.
2. J. W. CAHN, *Critical point wetting*, J. Chem. Phys., **66**, 3667–3672, 1977.
3. H. GOUIN, *Energy of interaction between solid surfaces and liquids*, J. Phys. Chem., **102**, 1212–1218, 1998.
4. P. GERMAIN, *La méthode des puissances virtuelles en mécanique des milieux continus*, J. de Mécanique, **12**, 235–274, 1973.
5. P. CASAL, *La théorie du second gradient et la capillarité*, Comptes Rendus Acad. Sc. Paris, **274**, 1571–1574, 1972.

6. P. CASAL, H. GOUIN, *Sur les interfaces liquide-vapeur non-isothermes*, J. de Mécanique Théorique et Appliquée, **7**, 689–718, 1988.
7. H. GOUIN, *Utilization of the second gradient theory in continuum mechanics to study the motion and thermodynamics of liquid-vapor interfaces*, Physicochemical Hydrodynamics – Interfacial Phenomena, **B**, **174**, 667–682, 1987.
8. F. DELL'ISOLA, W. KOSIŃSKI, *Deduction of thermodynamic balance law for bidimensional nonmaterial directed continua modelling interface layers*, Arch. Mech., **45**, 3, 333–359, 1993.
9. F. DELL'ISOLA, H. GOUIN, G. ROTOLI, *Nucleation of spherical shell-like interfaces by second gradient theory: numerical simulations*, Eur. J. Mech. B/Fluids, **15**, 545–568, 1996.
10. J. S. ROWLINSON, B. WIDOM, *Molecular theory of capillarity*, Clarendon Press, Oxford 1984.
11. P. SEPPECHER, *Equilibrium of a Cahn-Hilliard fluid on a wall: influence of the wetting properties of the film upon the stability of a thin film*, Eur. J. Mech. B/Fluids, **12**, 69–84, 1993.
12. J. SERRIN, *Mathematical principles of classical fluid mechanics*, [in:] Encyclopedia of Physics, S. FLÜGGE [Ed.], vol. VIII/1, Springer-Verlag, Berlin 1959.
13. R.A. TOUPIN, *Elastic materials with couple stresses*, Arch. Rat. Mech. Anal., **11**, 385–398, 1962.

L.M.M.T., FACULTÉ DES SCIENCES
UNIVERSITÉ D'AIX-MARSEILLE, CASE 322
Avenue Escadrille Normandie-Niemen
13397 Marseille Cedex 20, FRANCE
e-mail: henri.gouin@meca.u-3mrs.fr

and

INSTITUTE OF FUNDAMENTAL TECHNOLOGICAL RESEARCH
POLISH ACADEMY OF SCIENCES
e-mail: wkos@ippt.gov.pl

Received April 16, 1998.
