# Adiabatic waves along interfacial layers near the critical point

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**Abstract**

Near the critical point, isothermal interfacial zones are investigated starting from a non-local density of energy. From the equations of motion of thermocapillary fluids, we point out a new kind of adiabatic waves propagating along the interfacial layers. The waves are associated with the second derivatives of densities and propagate with a celerity depending on the proximity of the critical point. ***To cite this article: H. Gouin, C. R. Mecanique 332 (2004).***
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**Résumé**

**Ondes adiabatiques le long des interfaces près du point critique.** Près du point critique, les couches interfaciales sont modélisées à l'aide d'une densité d'énergie non locale. A partir des équations du mouvement des fluides thermocapillaires, nous mettons en évidence des ondes adiabatiques se propageant le long des couches interfaciales. Ces ondes associées aux dérivées secondes des densités se meuvent avec une célérité dépendant de la proximité du point critique. ***Pour citer cet article : H. Gouin, C. R. Mecanique 332 (2004).***
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## Version française abrégée

Le modèle le plus simple permettant de considérer les couches capillaires et les phases comme un unique milieu continu, consiste à prendre en compte une énergie comme la somme de deux termes : le premier correspond à l'énergie du milieu supposé uniforme et de composition égale à la composition locale, le second est associé à la non uniformité du fluide et exprimé par un développement en gradient de la masse volumique qui est limité au second ordre [1,2]. Ce modèle permet le prolongement au cas dynamique des études effectuées sur les systèmes en équilibre. L'énergie interne volumique du fluide est maintenant proposée sous la forme d'une densité $\alpha$ dépendant non seulement de grad $\rho$ mais aussi de grad $s$ où $\rho$ et $s$ notent respectivement la masse volumique et l'entropie

spécifique. Les milieux associés appelés *fluides thermocapillaires* [7] ont une densité d'énergie de la forme (1). Pour un fluide isotrope, l'énergie prend la forme (2) et l'équation du mouvement s'écrit sous les formes équivalentes (5) ou (6) dans lesquelles une entropie $h$ et une température $\theta$ dites *thermocapillaires* explicitées en (4) font intervenir deux nouveaux vecteurs $\boldsymbol{\Phi}$ and $\boldsymbol{\Psi}$ associés à la non homogénéité des zones interfaciales et donnés par (3). Une telle énergie interne associe dans les équations du mouvement et de l'énergie un tenseur des contraintes sphérique. Le cas des écoulements isentropiques associés à l'Éq. (7) correspond à la conservation de l'énergie (8). Les mouvements isothermes représentés par (9) et (10) ont comme cas particulier les équilibres isothermes entre phases.

Il est alors possible d'étudier les profils des densités dans les équilibres unidimensionnels correspondant aux zones interfaciales *planes*. Le choix d'une énergie interne thermocapillaire de la forme (11) associée à une énergie interne $\alpha$ du milieu supposé homogène ramène l'étude des zones interfaciales à l'analyse d'un système dynamique (12a), (12b) qui donne deux équations différentielles. L'analyse asymptotique de ce système au voisinage du point critique montre que la densité de masse *pilote* le système en ce sens que l'on est ramené à une décomposition dynamique représentée par le système (15a), (15b). L'intégration de ce système nous ramène simplement au cas d'un modèle ne faisant plus intervenir que grad $\rho$. On retrouve immédiatement à partir de (16), les résultats proposés par Rowlinson et Widom [6] pour le profil de la masse volumique, l'épaisseur de la couche interfaciale et la valeur de la tension superficielle des interfaces fluides au voisinage du point critique.

Il est maintenant possible d'étudier, dans les interfaces isothermes, les ondes d'accélération correspondant à des discontinuités faibles des mouvements isentropiques c'est-à-dire celles pour lequelle $\rho$, $s$, grad $\rho$ et grad $s$ sont continus à la traversée des surfaces d'onde. Un calcul *à la Hadamard* [11] est proposé. Il prend en compte l'équation de conservation de la masse (18), l'équation du mouvement sous la forme (5) et la condition de Rankine–Hugoniot associée à l'équation du mouvement écrite sous la forme équivalente (6). Il permet alors d'obtenir le système (23), (25), (27) de trois équations linéaires et homogènes relatif aux discontinuités des dérivées secondes à travers les surfaces d'onde (Section 4.1). La condition de compatibilité de ce système s'exprime par l'Éq. (28) qui donne ainsi la célérité de l'onde.

La relation (15a) issue du système dynamique (14a), (14b) obtenu par l'analyse asymptotique de la Section 3, permet d'expliciter la relation liant les gradients d'entropie et de masse volumique. Nous la calculons pour la valeur de la masse volumique critique. Nous en déduisons la valeur explicite de la célérité des ondes d'accélération cisaillées dans les interfaces fluides. Cette célérité exprimée par la relation (29) dépend des conditions thermodynamiques du point critique et de l'importance des coefficients associés aux termes représentant l'inhomogénéité du fluide dans la zone interfaciale. Elle est proportionnelle à $(T_c - T_0)^2$ où $T_0$ représente la valeur de la température dans les phases liquide et vapeur et $T_c$ note la température critique.

Les ondes solitaires dans la direction normale aux zones interfaciales ne dépendent pas du gradient d'entropie. Il n'en est pas de même des ondes isentropiques d'accélération qui se meuvent le long des interfaces : le fait que l'énergie interne dépend non seulement du gradient de masse volumique mais aussi du gradient d'entropie fait apparaître un nouveau type d'ondes qu'il est impossible de mettre en évidence dans les modèles plus simples ne faisant intervenir que le gradient de masse volumique. Ces ondes exceptionnelles au sens de Lax [12] nécessitent le cadre d'un modèle physique à au moins deux dimensions d'espace. Des expériences effectuées récemment dans des laboratoires embarqués dans des engins spatiaux et utilisant comme fluide test le gaz carbonique dans des conditions qui le placent au voisinage de son point critique, semblent montrer l'existence de telles ondes [13] et justifieraient alors le bien fondé du modèle de fluides thermocapillaires.

## 1. Introduction

To study capillary layers and bulk phases, the simplest model considers an energy as the sum of two terms: a first one corresponding to a medium with a uniform composition equal to the local one and a second one associated with the non-uniformity of the fluid [1,2]. The second term is approximated by a gradient expansion, typically

truncated to the second order. A representation of the energy near the critical point therefore allows the study of interfaces of non-molecular size. Obviously, the model is simpler than models associated with the renormalization-group theory [3]. Nevertheless, it has the advantage of extending easily well-known results for equilibrium cases to the dynamics of interfaces [4,5]. At equilibrium, Rowlinson and Widom [6] pointed out that the model can be extended by taking into account not only the strong variations of matter density through the interfacial layer but also the strong variations of entropy. In dynamics, for an *extended Cahn and Hilliard fluid*, the volumic internal energy $\varepsilon$ is proposed with a gradient expansion depending not only on $\operatorname{grad}\rho$ but also on $\operatorname{grad}s$ ($\rho$ is the matter density and $s$ the specific entropy):

$$\varepsilon = f(\rho, s, \operatorname{grad}\rho, \operatorname{grad}s) \tag{1}$$

The medium is then called a *thermocapillary fluid* [7]. Using an energy in the form (1), we have obtained the equations of conservative motions for nonhomogeneous fluid near its critical point [7–9].

The idea of studying interface motions as localized travelling waves in a multi-gradient theory is not new and can be traced throughout many problems of condensed matter and phase-transition physics [10]. In Cahn and Hilliard's model [2], the direction of solitary waves was along the gradient of density [4,10]. Here, adiabatic waves are considered and a new kind of waves appears. The waves are associated with the spatial second derivatives of entropy and matter density. For this new kind of adiabatic waves, the direction of propagation is normal to the gradient of densities. In the case of a thick interface, the waves are tangential to the interface and the wave celerity is expressed depending on thermodynamic conditions at the critical point.

## 2. Equations of thermocapillary fluid motions

The equations of motion are proposed in [7–9]. Due to the fact the fluid is isotropic, $\operatorname{grad}\rho$ and $\operatorname{grad}s$ are taken into account by their scalar products only. Let us denote

$$\beta = (\operatorname{grad}\rho)^2, \quad \chi = \operatorname{grad}\rho \cdot \operatorname{grad}s, \quad \gamma = (\operatorname{grad}s)^2$$

In variables $\rho, s, \beta, \chi, \gamma$

$$\varepsilon = g(\rho, s, \beta, \chi, \gamma) \tag{2}$$

The equations of thermocapillary fluids introduced two new vectors $\boldsymbol{\Phi}$ and $\boldsymbol{\Psi}$ such that:

$$\boldsymbol{\Phi} = C \operatorname{grad}\rho + D \operatorname{grad}s, \qquad \boldsymbol{\Psi} = D \operatorname{grad}\rho + E \operatorname{grad}s \tag{3}$$

with

$$C = 2\varepsilon_{,\beta}, \qquad D = \varepsilon_{,\chi}, \qquad E = 2\varepsilon_{,\gamma}$$

We denote

$$h = \varepsilon_{,\rho} - \operatorname{div}\boldsymbol{\Phi}, \qquad \theta = \frac{1}{\rho}(\varepsilon_{,s} - \operatorname{div}\boldsymbol{\Psi}) \tag{4}$$

In the case of classical compressible fluids, scalars $\varepsilon_{,\rho}$ and $(1/\rho)\varepsilon_{,s}$ are the specific enthalpy and the Kelvin temperature denoted by $T$. Look at two particular cases:

### 2.1. Conservative motions

We obtained [7] the equation of motion in the form:

$$\boldsymbol{\Gamma} = \theta \operatorname{grad}s - \operatorname{grad}(h + \Omega) \tag{5}$$

where $\boldsymbol{\Gamma}$ is the acceleration vector, $\Omega$ is the extraneous force potential. This equation is equivalent to the balance of momentum:

$$\frac{\partial}{\partial t}(\rho\mathbf{u}) + \mathrm{div}(\rho\mathbf{u} \otimes \mathbf{u} - \sigma) + \rho\,\mathrm{grad}\,\Omega = 0 \tag{6}$$

with $\sigma_i^j = -(P - \rho\,\mathrm{div}\,\boldsymbol{\Phi})\delta_i^j - \Phi^j\rho_{,i} - \Psi^j s_{,i}$ where $P = \rho\varepsilon_{,\rho} - \varepsilon$ (in the case of classical compressible fluids, $P$ denotes the pressure) and $\mathbf{u}$ is the fluid velocity. For conservative motions,

$$\frac{\mathrm{d}s}{\mathrm{d}t} = 0 \tag{7}$$

which is equivalent to the balance of energy

$$\frac{\partial e}{\partial t} + \mathrm{div}\big((e - \sigma)\mathbf{u}\big) - \mathrm{div}\,\mathbf{W} - \rho\frac{\partial\Omega}{\partial t} = 0 \tag{8}$$

with $\mathbf{W} = \frac{\mathrm{d}\rho}{\mathrm{d}t}\boldsymbol{\Phi} + \frac{\mathrm{d}s}{\mathrm{d}t}\boldsymbol{\Psi}$ and $e = \frac{1}{2}\rho\mathbf{u}^2 + \varepsilon + \rho\Omega$

### 2.2. Isothermal motions

We obtained [7] the equation of motion in the form:

$$\theta = T_0 \tag{9}$$

$$\boldsymbol{\Gamma} = -\,\mathrm{grad}(\mu + \Omega) \tag{10}$$

where $T_0$ is constant and $\mu = \varepsilon_{,\rho} - s\theta - \mathrm{div}\,\boldsymbol{\Phi}$ is the *chemical potential* of the thermocapillary fluid.

## 3. Liquid–vapor interface near its critical point

The critical point associated with the equilibrium of two bulks of a fluid corresponds to the limit of their coexistence. The thickness of the interface increases as the critical point is approached and it becomes infinite when the interface itself disappears. As its critical point is approached, the gradients of densities are then smooth. In the following, we consider the case when

$$\varepsilon = \alpha(\rho, \eta) + \frac{1}{2}\big(C(\mathrm{grad}\,\rho)^2 + 2D\,\mathrm{grad}\,\rho \cdot \mathrm{grad}\,s + E(\mathrm{grad}\,s)^2\big) \tag{11}$$

where $\alpha$ denotes the volumic internal energy of the fluid in uniform composition (let $\alpha(\rho, \eta)$ be an analytic function of the mass density $\rho$ and the entropy density $\eta \equiv \rho s$ as it might be given by a mean-field theory [6]), $C$, $D$, $E$ are constants and $CE - D^2 > 0$ (if $D = 0$ and $E = 0$, we are back to the Cahn and Hilliard model of capillarity [2]). Then $\alpha'_\eta = T$ and $\alpha'_\rho = \mu_0$ are respectively the Kelvin temperature and the chemical potential of the homogeneous fluid of matter density $\rho$ and entropy density $\eta$. At phase equilibrium, Eq. (9) is verified when $T_0$ is the temperature in the bulks. If we neglect the body forces, we obtain

$$D\Delta\rho + E\Delta s = \varepsilon'_s - \rho T_0 \tag{12a}$$

$$C\Delta\rho + D\Delta s = \varepsilon'_\rho - sT_0 - \mu_1 \tag{12b}$$

where $\mu_1$ is the value of $\mu_0$ in the liquid and the vapor bulks.

To be in accordance with Rowlinson and Widom ([6], p. 253), we consider a representation of $\alpha(\rho, \eta)$ associated with the coexistence curve in the form

$$\alpha(\rho, \eta) = \frac{B}{2A^2}\left(\big(A(\rho - \rho_c)^2 + \eta\big)^2 + \left(\eta + \frac{A^2}{B}(T_c - T_0)\right)^2\right) + \rho\mu_1 + \eta T_0 \tag{13}$$

Subscript $c$ and the two positive constants $A$ and $B$ are associated with the critical conditions. Moreover $s$, which is defined except to any additive constant, is chosen such that $s_c = 0$. System (12) yields

$$D\Delta\rho + E\Delta s = \frac{B}{A}\rho(\rho - \rho_c)^2 + 2\frac{B}{A^2}\rho^2 s + \rho(T_c - T_0)$$

$$C\Delta\rho + D\Delta s = 2B(\rho - \rho_c)^3 + 2\frac{B}{A}\rho s(\rho - \rho_c) + \frac{B}{A}(\rho - \rho_c)^2 s + 2\frac{B}{A^2}\rho s^2 + s(T_c - T_0)$$

The equations of the coexistence curve at $T = T_0$ are related with $\Delta\rho = 0$ and $\Delta s = 0$. They are as in [6], pp. 253–254: in the bulks, near the critical point $\rho - \rho_c \sim cte(T_c - T_0)^{1/2}$, $s \sim cte(T_c - T_0)$; then in the bulks $A(\rho - \rho_c)^2 + \rho s = 0$ and $\rho s + (A^2/B)(T_c - T_0) = 0$.

In one-dimensional problems, $\rho = \rho(y)$, $s = s(y)$. To consider the respective order of magnitude of the densities and the physical scales associated with the interfacial sizes, we look at the change of variables

$$T_c - T_0 = \varepsilon\Upsilon, \quad y = \varepsilon^n Y, \quad \rho(y) - \rho_c = \varepsilon^{1/2}R(Y), \quad s(y) = \varepsilon S(Y)$$

where $0 < \varepsilon \ll 1$, and $n$ is constant. The main part of system (12) leads to

$$\varepsilon^{-2n}\left(D\varepsilon^{1/2}\frac{d^2 R}{dY^2} + E\varepsilon\frac{d^2 S}{dY^2}\right) = \varepsilon\left(\frac{B}{A}\rho R^2 + 2\frac{B}{A^2}\rho^2 S + \rho\Upsilon\right) \tag{14a}$$

$$\varepsilon^{-2n}\left(C\varepsilon^{1/2}\frac{d^2 R}{dY^2} + D\varepsilon\frac{d^2 S}{dY^2}\right) = \varepsilon^{3/2}\left(2BR^3 + 2\frac{B}{A}\rho RS\right) \tag{14b}$$

Then $n = -\frac{1}{2}$ and in this asymptotic analysis, if $''$ denotes the second derivative with respect to the space variable $y$, system (12) yields an approximation where the entropy density $\eta$ varies with the matter density $\rho$ as it would be in a bulk phase [6], p. 254:

$$2\eta = \frac{A^2}{B}(T_0 - T_c) - A(\rho - \rho_c)^2 \tag{15a}$$

$$C\rho'' = 2B(\rho - \rho_c)^3 + 2\frac{B}{A}\eta(\rho - \rho_c) \tag{15b}$$

and consequently by elimination of $s$ between (15a) and (15b), we obtain

$$C\rho'' = B(\rho - \rho_c)^3 - A(T_c - T_0)(\rho - \rho_c) \tag{16}$$

and for planar liquid–vapor interfaces,

$$\frac{1}{2}C\rho'^2 = \left(\frac{\sqrt{B}}{2}(\rho - \rho_c)^2 - \frac{A}{2\sqrt{B}}(T_c - T_0)\right)^2 \tag{17}$$

We are back to the classical van der Waals theory for mass density profile in the interfacial layer (see [6], pp. 250–251).

## 4. Weak discontinuity in conservative motions

### 4.1. Conditions of a weak discontinuity

In a fixed coordinate system, to describe the fluid motion, we refer to the coordinates $\mathbf{x} \equiv (x^1, x^2, x^3)$ as the particle position (Eulerian variables). We denote by $\mathbf{z} = \binom{t}{\mathbf{x}}$ the time–space variables; $\mathbf{V} \equiv \binom{1}{\mathbf{u}}$ is the time–space velocity. Let us consider a mobile surface $\Sigma_t$ defined in the physical space occupied by the fluid, we denote by $g$

the celerity of $\Sigma_t$, $\mathbf{n}$ its normal vector, $\mathbf{N} = \binom{-g}{\mathbf{n}}$; $v = \mathbf{N}^*\mathbf{V} \equiv \mathbf{n}^*\mathbf{u} - g$ is the fluid velocity with respect to $\Sigma_t$ ($-v$ is the celerity of $\Sigma_t$ with respect to the fluid) and $\mathbf{n}^*$ is the transposed of $\mathbf{n}$.

To Eq. (6) of motion, we have to add the equation of balance of mass

$$\frac{\partial \rho}{\partial t} + \mathrm{div}(\rho \mathbf{u}) = 0 \tag{18}$$

Eq. (7) of conservation of the entropy and relation (13).

Due to the important fact that the first discontinuities of $\rho$ and $s$ do not exist in thermocapillary fluid motions, weak discontinuities of isentropic motions correspond to $\rho, s, \partial\rho/\partial\mathbf{x}, \partial s/\partial\mathbf{x}$, continuous through the wave surfaces. As in [11], we denote by [] the jump of a tensorial quantity through a surface of discontinuity $\Sigma_t$. The jump of a spatial derivative of a continuous quantity is colinear to the normal vector to the wave surface; as in Hadamard's tensorial framework, there exist two scalar fields $\lambda_1, \lambda_2$ on $\Sigma_t$, such that

$$\left[\frac{\partial \rho}{\partial \mathbf{z}}\right] = 0 \Rightarrow \left[\frac{\partial}{\partial \mathbf{z}}\left(\frac{\partial \rho}{\partial \mathbf{z}}\right)^*\right] = \lambda_1 \mathbf{N}\mathbf{N}^* \Rightarrow \left[\frac{\partial}{\partial \mathbf{x}}\left(\frac{\partial \rho}{\partial \mathbf{x}}\right)^*\right] = \lambda_1 \mathbf{n}\mathbf{n}^* \tag{19a}$$

$$\left[\frac{\partial s}{\partial \mathbf{z}}\right] = 0 \Rightarrow \left[\frac{\partial}{\partial \mathbf{z}}\left(\frac{\partial s}{\partial \mathbf{z}}\right)^*\right] = \lambda_2 \mathbf{N}\mathbf{N}^* \Rightarrow \left[\frac{\partial}{\partial \mathbf{x}}\left(\frac{\partial s}{\partial \mathbf{x}}\right)^*\right] = \lambda_2 \mathbf{n}\mathbf{n}^* \tag{19b}$$

and consequently

$$\lambda_1 = [\Delta\rho] \quad \text{and} \quad \lambda_2 = [\Delta s] \tag{20}$$

From $[\mathbf{V}] = 0$, we deduce $[\partial\mathbf{V}/\partial\mathbf{z}] = \boldsymbol{\Xi}\mathbf{N}^*$ with $\mathbf{N}^* = (-g, \mathbf{n}^*)$ and $\boldsymbol{\Xi} = \binom{0}{\mathbf{H}}$, where $\mathbf{H}$ is a 3-vector field on $\Sigma_t$. Then,

$$[\Gamma] = \left[\frac{\partial \mathbf{u}}{\partial \mathbf{z}}\right]\mathbf{V} = \mathbf{H}\mathbf{N}^*\mathbf{V} \equiv v\mathbf{H}$$

Equation of mass conservation (18) is equivalent to

$$\frac{\partial \rho}{\partial \mathbf{z}}\mathbf{V} + \rho \, \mathrm{Tr}\left(\frac{\partial \mathbf{V}}{\partial \mathbf{z}}\right) = 0$$

where Tr denotes the trace operator. Then, $[\mathrm{Tr}(\partial\mathbf{V}/\partial\mathbf{z})] = 0$ and consequently,

$$\mathbf{n}^*\mathbf{H} = 0 \tag{21}$$

Eq. (7) of conservation of entropy implies

$$\frac{\partial}{\partial \mathbf{z}}\left(\frac{\mathrm{d}s}{\mathrm{d}t}\right) = 0 \quad \Leftrightarrow \quad \frac{\partial}{\partial \mathbf{z}}\left(\frac{\partial s}{\partial \mathbf{z}}\mathbf{V}\right) = 0$$

Then,

$$\left[\left(\frac{\partial}{\partial \mathbf{z}}\left(\frac{\partial s}{\partial \mathbf{z}}\right)^*\right)^*\mathbf{V} + \left(\frac{\partial \mathbf{V}}{\partial \mathbf{z}}\right)^*\left(\frac{\partial s}{\partial \mathbf{z}}\right)^*\right] = 0$$

Due to the fact that $\frac{\partial}{\partial \mathbf{z}}(\frac{\partial s}{\partial \mathbf{z}})^*$ is a symmetric tensor,

$$\lambda_2 \mathbf{N}\mathbf{N}^*\mathbf{V} + \mathbf{N}\boldsymbol{\Xi}^*\left(\frac{\partial s}{\partial \mathbf{z}}\right)^* = 0 \quad \Leftrightarrow \quad \mathbf{N}\left(\lambda_2 v + \frac{\partial s}{\partial \mathbf{x}}\mathbf{H}\right) = 0$$

or,

$$\lambda_2 v + \frac{\partial s}{\partial \mathbf{x}}\mathbf{H} = 0 \tag{22}$$

From Rankine–Hugoniot condition associated to Eq. (6), we obtain the compatibility condition: $[-g\rho\mathbf{u}^* + \rho\mathbf{n}^*\mathbf{u}\mathbf{u}^* - \mathbf{n}^*\sigma] = 0$, and the continuity of $\rho$, $\partial\rho/\partial\mathbf{x}$, $s$, $\partial s/\partial\mathbf{x}$, yields $[\operatorname{div}\boldsymbol{\Phi}] = 0$ or $[C\Delta\rho + D\Delta s] = 0$ which is equivalent to

$$C\lambda_1 + D\lambda_2 = 0 \tag{23}$$

Consequently, there exists a scalar field $\lambda_3$ on $\Sigma_t$ such that

$$\left[\frac{\partial}{\partial\mathbf{x}}(C\Delta\rho + D\Delta s)\right] = \lambda_3\mathbf{n}^* \tag{24}$$

Equation of motion (5) yields

$$[\Gamma] = [\theta]\operatorname{grad} s - \lambda_3\mathbf{n}, \quad \text{or} \quad \rho v\mathbf{H} = -(D\lambda_1 + E\lambda_2)\operatorname{grad} s - \rho\lambda_3\mathbf{n}$$

Projecting on the normal and tangent plane to $\Sigma_t$ and taking relation (21) into account, we obtain

$$D(\mathbf{n}^*\operatorname{grad} s)\lambda_1 + E(\mathbf{n}^*\operatorname{grad} s)\lambda_2 + \rho\lambda_3 = 0 \tag{25}$$

$$\rho v\mathbf{H} = -(D\lambda_1 + E\lambda_2)\operatorname{grad}_{\text{tg}} s \tag{26}$$

where $\operatorname{grad}_{\text{tg}} s$ denotes the tangential part of $\operatorname{grad} s$ in $\Sigma_t$. Elimination of $\mathbf{H}$ in the relation (26) comes from relation (22), and we get

$$D(\operatorname{grad}_{\text{tg}} s)^2\lambda_1 + \left(E(\operatorname{grad}_{\text{tg}} s)^2 - \rho v^2\right)\lambda_2 = 0 \tag{27}$$

Consequently, we obtain the system (23), (25), (27) of three homogeneous linear equations with respect to the variables $\lambda_1$, $\lambda_2$, $\lambda_3$. The compatibility of the three equations yields

$$\rho v^2 = \frac{(CE - D^2)(\operatorname{grad}_{\text{tg}} s)^2}{C} \tag{28}$$

### 4.2. Celerity of isentropic waves of acceleration

The temperature in liquid and vapor bulks is $T_0$. Then relation (15a) yields

$$\operatorname{grad}\left(A(\rho - \rho_c)^2 + 2\rho s\right) = 0 \quad \Leftrightarrow \quad A(\rho - \rho_c)\operatorname{grad}\rho + \operatorname{grad}\rho s = 0$$

The value $\rho = \rho_c$ of the matter density in the interface corresponds to the maximum value of $\operatorname{grad}\rho$. The matter density $\rho_c$ is characteristic of the interfacial matter. For such a value, $\operatorname{grad}\rho s = 0$ and $s = (A^2/(2B\rho_c))(T_0 - T_c)$.

Consequently, $\operatorname{grad} s = (A^2/(2B\rho_c^2))(T_c - T_0)\operatorname{grad}\rho$, and

$$v^2 = \frac{(CE - D^2)A^4(\operatorname{grad}_{\text{tg}}\rho)^2(T_c - T_0)^2}{4CB^2\rho_c^5}$$

For waves shearing the interfacial layer, due to relation (17) we obtain, when $\rho = \rho_c$, $C(\operatorname{grad}_{\text{tg}}\rho)^2 = (A^2/(2B))(T_c - T_0)^2$, and consequently,

$$v^2 = \frac{(CE - D^2)A^6(T_c - T_0)^4}{8C^2B^3\rho_c^5} \tag{29}$$

In the interfacial layer, $\operatorname{grad}\rho$ is normal to iso-density surfaces. The isentropic waves of acceleration associated with a weak discontinuity shear the interfacial layer. The wave celerity which is proportional to $(T_c - T_0)^2$, vanishes at the critical point and can be calculated numerically by means of a state equation.

## 5. Results and discussion

Near the critical point, for thermocapillary fluids, the variations of matter density lead to the variations of entropy. This extension of Cahn and Hilliard fluids seems at first sight purely formal and at equilibrium yields same results as the classical van der Waals model does [1]. In dynamics, motions in the normal direction to fluid interfaces (as solitary waves) are not involved in an additive dependance of the entropy gradient. In this paper, we see that the dependance of entropy gradient is necessary for isentropic waves of acceleration along the interfaces: the fact that the internal energy depends not only on the gradient of matter density but also on the gradient of entropy, yields a new kind of waves which does not appear in the simpler models. It is easy to see they are exceptional waves in the sense of Lax [12] and they appear only in, at least, two-dimension spaces. Recent experiments in space laboratories, for carbonic dioxide near its critical point have showed the possibility of such waves [13] and should justify the well-founded of the thermocapillary fluid model.

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