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THERMOCAPILLARY FLUID AND ADIABATIC WAVES NEAR THE CRITICAL POINT

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Isothermal interfacial zones are investigated starting from a local energy which can be considered as the sum of two terms: 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. The additional term can be 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. Capillary layer and bulk phases are not considered independently. Obviously, this model is simpler than models associated with the renormalization-group theory. Nevertheless, it has the advantage of extending easily well-known results for equilibrium cases to the dynamics of interfaces. The equation of state of a one-component system may be expressed as a relation among the energy, entropy and matter density, α , s and ρ in the form $\alpha = \alpha(\rho, s)$. Now, let $\alpha(\rho, s)$ be the analytic α as it might be given by a mean-field theory. In the simplest case, in an *extended van der Waals theory*¹⁸, the volume internal energy ε is proposed with a gradient expansion depending not only on $\text{grad } \rho$ but also on $\text{grad } s$ (the associated fluid is called thermocapillary fluid³):

$$\varepsilon = f(\rho, s, \text{grad } \rho, \text{grad } s) \quad (1)$$

With an energy in the form (1), we obtain the equations of motion of conservative movements for nonhomogeneous fluid near its critical point. For such a medium, it is not possible to obtain shock waves. 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 physics⁸. 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. In Cahn and Hilliard's model¹, the direction of solitary waves was along the gradient of 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.

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1. Equations of motion of thermocapillary fluids

1.1. Conservative motions

For conservative motions of perfect fluids -that is to say without heat fluxes or viscosity- the specific entropy of each particle remains constant along trajectories ($\dot{s} = 0$, where $\dot{\cdot}$ denotes the material derivative). A convenient method allowing to obtain the equations of motion comes from the Hamilton principle. The notations are in Serrin¹⁴: in a fixed coordinate system, the components of a vector (covector) \mathbf{a} are denoted by a^i , (a_i), where $i = 1, 2, 3$. In order to describe the fluid motion analytically, we refer to the coordinates $\mathbf{x} \equiv (x^1, x^2, x^3)$ as the particle's position (Eulerian variables). The corresponding reference position is denoted by $\mathbf{X} \equiv (X^1, X^2, X^3)$ (Lagrangian variables). The motion of a fluid is classically represented by the transformation $\mathbf{x} = \varphi(t, \mathbf{X})$ or $x^i = \varphi^i(t, \mathbf{X})$, where t is the time. It is assumed that φ possesses an inverse $\mathbf{X} = \phi(t, \mathbf{x})$ and continuous derivatives up to the second order except at certain surfaces.

We denote by $\mathbf{z} = \begin{pmatrix} t \\ \mathbf{x} \end{pmatrix}$ the time-space variables; $\mathbf{u} \equiv \frac{\partial \varphi}{\partial t}(t, \mathbf{X})$ and

$\mathbf{V} \equiv \begin{pmatrix} 1 \\ \mathbf{u} \end{pmatrix}$ are respectively the velocity and the time-space velocity. Let

us consider a mobile surface Σ_t defined in the physical space D_t occupied by the fluid. Let us denote by g the celerity of Σ_t , \mathbf{n} its normal vector,

$\mathbf{N} = \begin{pmatrix} -g \\ \mathbf{n} \end{pmatrix}$ and $v = \mathbf{N}^* \mathbf{V} \equiv \mathbf{n}^* \mathbf{u} - g$ the fluid velocity with respect to Σ_t ,

where $*$ is the transposition on D_t .

The Lagrangian of a thermocapillary fluid is written

$$L = \frac{1}{2} \rho \mathbf{u}^* \mathbf{u} - \varepsilon - \rho \Omega,$$

where Ω is the extraneous force potential defined as a function of \mathbf{z} and ε is the internal energy per unit volume. Between times t_1 and t_2 , Hamilton's action is

$$a = \int_{t_1}^{t_2} \int_{D_t} L \, dv dt$$

A variation of the particle motion comes from a family of virtual motions $\mathbf{X} = \psi(t, \mathbf{x}, r)$ where r denotes a small parameter close to 0. The real motion is associated with $r = 0$ ($\psi(t, \mathbf{x}, 0) = \phi(t, \mathbf{x})$) and a virtual displacement is expressed in the form⁷

$$\delta \mathbf{X} = \left(\frac{\partial \psi}{\partial r} \right)_{r=0} \quad (2)$$

Expression (2) corresponds to the dual of the variation given by Serrin¹⁴ in page 145. The density and the specific entropy verify respectively

$$\rho \det F = \rho_0(X), \quad (3)$$

$$s = s_0(X), \quad (4)$$

where ρ_0 and (for conservative motions) s_0 are defined into a reference space D_0 and at time t fixed, F is the Jacobian of φ . If ε given by relation (1) is differentiable,

$$\delta \varepsilon = \varepsilon_{,\rho} \delta \rho + \varepsilon_{,s} \delta s + \Phi^i \delta \rho_{,i} + \Psi^i \delta s_{,i},$$

and consequently, the theory introduces two new vectors Φ and Ψ such that :

$$\Phi^i = \varepsilon_{,\rho,i} \quad \text{and} \quad \Psi^i = \varepsilon_{,s,i}$$

(In the case of compressible fluids, scalars $\varepsilon_{,\rho}$ and $(1/\rho) \varepsilon_{,s}$ are the specific enthalpy and the Kelvin temperature).

Due to the fact the fluid is isotropic, grad ρ and grad s are taken into account by their scalar products only¹⁵. Let us denote

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

and in variables $\rho, s, \beta, \chi, \gamma$,

$$\varepsilon = g(\rho, s, \beta, \chi, \gamma)$$

Consequently,

$$\Phi = C \text{ grad } \rho + D \text{ grad } s, \quad \Psi = D \text{ grad } \rho + E \text{ grad } s, \quad (5)$$

with

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

Variations of Hamilton's action are deduced from classical method of variational calculus⁷,

$$\begin{aligned} \delta a = \int_{t_1}^{t_2} \int_{D_t} & \left(\frac{1}{2} \mathbf{u}^* \mathbf{u} \delta \rho + \rho \mathbf{u}^* \delta \mathbf{u} - \varepsilon_{,\rho} \delta \rho - \varepsilon_{,s} \delta s \right. \\ & \left. - \mathbf{\Phi}^* \delta \text{grad } \rho - \mathbf{\Psi}^* \delta \text{grad } s - \Omega \delta \rho \right) dv dt \end{aligned}$$

Due to the definition of virtual displacement in (2),

$$\delta \text{grad } \rho = \text{grad } \delta \rho, \quad \delta \text{grad } s = \text{grad } \delta s \quad \text{and} \quad \delta \mathbf{u} = -F \dot{\delta \mathbf{X}}$$

Due to the fact the virtual displacement $\delta \mathbf{X}$ and its derivatives are assumed null at the boundary of D_t , integration by parts using Stokes' formula yields

$$\begin{aligned} \delta a = \int_{t_1}^{t_2} \int_{D_t} & \left(\left(\frac{1}{2} \mathbf{u}^* \mathbf{u} - \varepsilon_{,\rho} + \text{div } \mathbf{\Phi} - \Omega \right) \delta \rho \right. \\ & \left. + \left(\text{div } \mathbf{\Psi} - \varepsilon_{,s} \right) \delta s + \rho \mathbf{u}^* F \delta \mathbf{X} \right) dv dt \end{aligned}$$

Taking into account relations⁷

$$\delta \rho = \rho \text{div}_0 \delta \mathbf{X} + \frac{1}{\det F} \frac{\partial \rho_0}{\partial \mathbf{X}} \delta \mathbf{X}, \quad (6)$$

where div_0 denotes the divergence operator in D_0 and

$$\delta s = \frac{\partial s_0}{\partial \mathbf{X}} \delta \mathbf{X}, \quad (7)$$

we get finally

$$\delta a = \int_{t_1}^{t_2} \int_{D_0} \rho_0 \left(\mathbf{u}^* F - \text{grad}_0 m - \theta \text{grad}_0 s_0 \right) \delta \mathbf{X} dv_0 dt$$

where grad_0 is the gradient in D_0 , and

$$\theta = \frac{1}{\rho} (\varepsilon_{,s} - \text{div } \mathbf{\Psi}), \quad h = \varepsilon_{,\rho} - \text{div } \mathbf{\Phi}, \quad m = \frac{1}{2} \mathbf{u}^* \mathbf{u} - h - \Omega$$

Then, Hamilton's principle yields

$$\mathbf{u}^* F = \text{grad}_0 m + \theta \text{grad}_0 s_0$$

Let us note that

$$\left(\mathbf{\Gamma}^* + \mathbf{u}^* \frac{\partial \mathbf{u}}{\partial \mathbf{x}} \right) F = \mathbf{u}^* F,$$

where $\mathbf{\Gamma}$ is the acceleration vector; we obtain the equation of motion in the form

$$\mathbf{\Gamma} = \theta \text{grad } s - \text{grad}(h + \Omega), \quad (8)$$

which is the extension of relation (29.8) in Serrin¹⁴. It is easy to prove that by algebraic calculus, this equation is equivalent to the balance of momentum^{3,4}

$$\frac{\partial}{\partial t} (\rho \mathbf{u}^*) + \text{div}(\rho \mathbf{u} \mathbf{u}^* - \sigma) + \rho \text{grad } \Omega = 0 \quad (9)$$

with $\sigma_i^j = -(P - \rho \text{div } \Phi) \delta_i^j - \Phi^j \rho_{,i} - \Psi^j s_{,i}$ where $P = \rho \varepsilon_{,\rho} - \varepsilon$ (in the case of compressible fluids, P denotes the pressure).

Relation $\dot{s} = 0$ is equivalent to the balance of energy^{3,4}

$$\frac{\partial e}{\partial t} + \text{div}((e - \sigma) \mathbf{u}) - \text{div } \mathbf{U} - \rho \frac{\partial \Omega}{\partial t} = 0$$

with $\mathbf{U} = \dot{\rho} \Phi + \dot{s} \Psi$ and $e = \frac{1}{2} \rho \mathbf{u}^* \mathbf{u} + \varepsilon + \rho \Omega$.

1.2. Properties of conservation for isentropic thermocapillary fluids

Conclusions obtained in (2,14) are easily extended to thermocapillary fluids.

They are deduced from Eq. (8). Let us recall the main results: $J = \oint_C \mathbf{u}^* d\mathbf{x}$ denotes the circulation of the velocity on a closed curve convected by the fluid. Then,

$$\frac{dJ}{dt} = \oint_C \theta ds \quad (10)$$

We obtain:

Kelvin's circulation theorem: the circulation of the velocity on a closed and isentropic curve is constant.

For any motion of isentropic thermocapillary fluid, it is possible to introduce scalar potentials with the following evolutions² :

$$\dot{\kappa} = m \equiv \frac{1}{2} \mathbf{u}^* \mathbf{u} - h - \Omega, \quad \dot{\tau} = 0, \quad \dot{\xi} = 0, \quad \dot{\zeta} = 0, \quad \dot{s} = 0, \quad (11)$$

such that the velocity field is written

$$\mathbf{u} = \text{grad } \kappa + \xi \text{grad } s + \tau \text{grad } \zeta \quad (12)$$

From eqs. (11) and (12), one deduces the classification given by Casal² for conservative flow of perfect fluids.

Oligotropic motions: they are motions for which iso-entropy surfaces are surfaces of vorticity. The circulation of the velocity on an isentropic closed curve convected by the fluid is null. Eq. (12) yields

$$\mathbf{u} = \text{grad } \kappa + \xi \text{ grad } s$$

Homentropic motions: s is constant in the fluid and Eq. (12) yields

$$\mathbf{u} = \text{grad } \kappa + \tau \text{ grad } \varsigma$$

The Cauchy theorem is extended without difficulty:

$$\frac{d}{dt} \left(\frac{\text{rot } \mathbf{u}}{\rho} \right) = \frac{\partial \mathbf{u}}{\partial \mathbf{x}} \frac{\text{rot } \mathbf{u}}{\rho}$$

If $H = \frac{1}{2} \mathbf{u}^* \mathbf{u} + h + \Omega$, we deduce from Eq. (8), the extended Crocco-Vazsonyi equation for steady thermocapillary fluid motions :

$$\text{rot } \mathbf{u} \times \mathbf{u} = \theta \text{ grad } s - \text{grad } H$$

Conservation laws expressed with Kelvin's theorems are associated to the group of permutation of particles of the same entropy. This group keeps the equations of motion invariant. As in ⁽⁶⁾ it is possible to associate an expression of the Noether theorem to this group. It is natural to conjecture such results for general fluids endowed with an internal energy which is a functional of matter and entropy densities.

1.3. Isothermal motions

Now, let us consider the case when only the total variation of the total entropy in D_t is zero³ (virtual displacements $\delta \mathbf{X}$ conserve the total entropy of D_t). Then,

$$\delta \int_{D_t} \rho s \, dv = 0$$

There exists a constant Lagrange multiplier T_0 such that the new Lagrangian

$$L = \frac{1}{2} \rho \mathbf{u}^* \mathbf{u} - \varepsilon - \rho \Omega + T_0 \rho s$$

yields

$$\delta a = \int_{t_1}^{t_2} \int_{D_t} \delta \left(\frac{1}{2} \rho \mathbf{u}^* \mathbf{u} - \varepsilon - \rho \Omega + T_0 \rho s \right) \, dv dt = 0$$

and consequently, as in section 1.1,

$$\begin{aligned} \delta a = \int_{t_1}^{t_2} \int_{D_t} & \left(\frac{1}{2} \mathbf{u}^* \mathbf{u} - \varepsilon_{,\rho} + T_0 s + \operatorname{div} \mathbf{\Phi} - \Omega \right) \delta \rho + \\ & + \left(\operatorname{div} \mathbf{\Psi} - \varepsilon_{,s} + T_0 \rho \right) \delta s + \rho \mathbf{u}^* \hat{F} \delta \mathbf{X} \, dv dt = 0 \end{aligned}$$

Here δs is any scalar field in D_t and $\delta \rho$ is given by relation (6). Finally, we obtain

$$\theta = T_0, \quad (13a)$$

$$\mathbf{\Gamma} = - \operatorname{grad}(\mu + \Omega), \quad (13b)$$

where $\mu = \varepsilon_{,\rho} - T_0 s - \operatorname{div} \mathbf{\Phi}$ is the *chemical potential* of the thermocapillary fluid. Eqs (13a), (13b) are the equations of motion of an isothermal capillary fluid. Let us remark that we obtain also *Kelvin's circulation theorem*: The circulation of the velocity on a closed and isotherm curve is constant.

2. 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 interface between the phases disappears when that point is reached. The thickness of the interface increases as the critical point is approached and it becomes infinite when the interface itself disappears. Much of what has been done on the theory of the near-critical interface has been within the framework of the van der Waals theory¹⁸, so much the present understanding of the properties of those interfaces comes from that theory or from suitable extended version of it¹². As its critical point is approached, the gradients of densities are then small. The present point of view (the interfacial region may be treated as matter in bulk, with local energy density that is that of a uniform fluid of composition equal to the local one, with an additional term arising from the non-uniformity, expressed by a gradient expansion truncated in second order) is then most likely to be successful and even qualitatively accurate. In the following, we consider the case when

$$\varepsilon = \rho \alpha(\rho, s) + \frac{1}{2} \left(C (\operatorname{grad} \rho)^2 + 2D \operatorname{grad} \rho \cdot \operatorname{grad} s + E (\operatorname{grad} s)^2 \right) \quad (14)$$

where α denotes the specific internal energy of the fluid in uniform composition, 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 capillarity¹. If not, we deduce

$$h = h_0 - (C \Delta \rho + D \Delta s), \quad \theta = T - \frac{1}{\rho} (D \Delta \rho + E \Delta s),$$

where $h_0 \equiv \alpha + \rho \alpha'_\rho$ and $T \equiv \alpha'_s$ are respectively the specific enthalpy and the Kelvin temperature of the homogeneous fluid of matter density ρ and specific entropy s . Let us note that vectors Φ and Ψ are always given by expression (5), but here coefficients C , D and E are constant.

At phase equilibrium, Eq. (13a) is verified when T_0 is the temperature in the bulks. If we neglect the body forces and denote $\mu_0 \equiv \alpha + \rho \alpha'_\rho - s T_0$, we obtain

$$C \Delta \rho + D \Delta s = \mu_0 - \mu_1, \quad (15a)$$

$$D \Delta \rho + E \Delta s = \rho (T - T_0), \quad (15b)$$

where $\mu_1 = \mu(\rho_l, s_l) = \mu(\rho_v, s_v)$ is constant (ρ_l, s_l, ρ_v, s_v are the densities in the liquid and the vapor bulks). In one-dimensional problems, $\rho = \rho(y)$ and equations of equilibrium are associated with the system

$$C \rho'' + D s'' = \varepsilon'_\rho - s T_0 - \mu_1, \quad (16a)$$

$$D \rho'' + E s'' = \varepsilon'_s - \rho T_0, \quad (16b)$$

where $''$ denotes the second derivative with respect to the space variable y . Near the critical point of the fluid, we use the representation of $\rho \alpha(\rho, s)$ in relation (14) in the form

$$\rho \alpha = \frac{B}{2A^2} \left(\left(A(\rho - \rho_c)^2 + \eta \right)^2 + \eta^2 \right) + \mu_c \rho + T_c \eta - p_c \quad (17)$$

given by Rowlinson and Widom in ⁽¹²⁾ when $\eta = \rho s$ is the entropy per unit volume in which $s_c = 0$, A and B are two positive constants associated with the critical conditions and μ_c , T_c , p_c are respectively the values of the chemical potential, the temperature and the pressure at the critical point. It is easy to verify that this expression is equivalent to the chemical potential μ_0 of a compressible fluid (case when $C = D = E = 0$) in the form :

$$\mu_0(\rho, T_0) = \mu_c + B (\rho - \rho_c)^3 - A (T_0 - T_c)(\rho - \rho_c),$$

where μ_c is the value of μ_0 for the critical conditions.

2.1. Asymptotic analysis of system (16) near the critical point

Due to relation (17), system (16) yields,

$$\begin{aligned} C \rho'' + D s'' &= 2B(\rho - \rho_c)^3 + 2\frac{B}{A}\rho s(\rho - \rho_c) + \frac{B}{A}(\rho - \rho_c)^2 s \\ &\quad + 2\frac{B}{A^2}\rho s^2 + (T_c - T_0)s + \mu_c - \mu_1, \\ D \rho'' + E s'' &= \frac{B}{A}\rho(\rho - \rho_c)^2 + 2\frac{B}{A^2}\rho^2 s + (T_c - T_0)\rho \end{aligned}$$

To consider the physical scales associated with the interfacial sizes, we look at the change of variables

$$Y = \epsilon y, \quad \rho(y) - \rho_c = \epsilon^{n_1} R(Y), \quad s(y) = \epsilon^{n_2} S(Y),$$

where $0 < \epsilon \ll 1$, and n_1, n_2 are two positive constants. We suppose the coefficients C, D and E to have finite, non-vanishing limiting values at the critical point. Then the main part of system (16) leads to

$$\begin{aligned} \epsilon^2 \left(C\epsilon^{n_1} \frac{d^2 R}{dY^2} + D\epsilon^{n_2} \frac{d^2 S}{dY^2} \right) &= \epsilon^{3n_1} 2B R^3 + \epsilon^{n_1+n_2} 2\frac{B}{A}\rho_c R S \\ &\quad \epsilon^{2n_1+n_2} \frac{B}{A} R^2 S + \epsilon^{2n_2} 2\frac{B}{A^2}\rho_c S^2 + \epsilon^{n_2} (T_c - T_0) S + \mu_c - \mu_1, \\ \epsilon^2 \left(D\epsilon^{n_1} \frac{d^2 R}{dY^2} + E\epsilon^{n_2} \frac{d^2 S}{dY^2} \right) &= \epsilon^{2n_1} \frac{B}{A}\rho_c R^2 + \epsilon^{n_2} 2\frac{B}{A^2}\rho_c^2 S + (T_c - T_0)\rho_c \end{aligned}$$

It is easy to verify that the solution is associated with $n_1 = 1, n_2 = 2$ and $\mu_c = \mu_1$. Near the critical point, in densities ρ, s and variable y , system (16) leads to an approximation in the form :

$$C \rho'' = \varepsilon'_\rho - s T_0 - \mu_1, \quad (18a)$$

$$\varepsilon'_s - \rho T_0 = 0 \quad (18b)$$

By other arguments, this asymptotic analysis gives the same results as in ⁽¹²⁾, page 254, where Rowlinson and Widom compared the magnitudes of different terms in a system similar to system (16): the magnitude of $D s''$ is negligible compared with the typical magnitude of $C \rho''$ and the magnitude of $D \rho'' + E s''$ is negligible with respect to the magnitude of $\varepsilon'_s - \rho T_0$.

2.2. Integration of system (16) in the approximation of the critical point

The approximation of the system (16) yields Eq. (18b) which is equivalent to $\theta = T_0$ and consequently,

$$2 \rho s = \frac{A^2}{B} (T_0 - T_c) - A (\rho - \rho_c)^2 \quad (19)$$

Taking Eq. (18a) into account, we obtain

$$C \rho'' = B (\rho - \rho_c)^3 - A (T_c - T_0)(\rho - \rho_c) + \mu_c - \mu_1 \quad (20)$$

and in the following $\mu_1 = \mu_c$ such that Eq. (20) is the classical equation of the density profile of a liquid-vapor interface¹². Integration of Eq. (20) yields

$$\frac{1}{2} C \rho'^2 = \frac{B}{4} (\rho - \rho_c)^4 - \frac{A}{2} (T_c - T_0)(\rho - \rho_c)^2 + f_0,$$

where f_0 is a constant which verifies for a planar liquid-vapor interface

$$f_0 = \frac{A^2}{4B} (T_c - T_0)^2,$$

and we obtain

$$\frac{1}{2} C \rho'^2 = \left(\frac{\sqrt{B}}{2} (\rho - \rho_c)^2 - \frac{A}{2\sqrt{B}} (T_c - T_0) \right)^2 \quad (21)$$

Eq. (21) yields the profile of matter density in the interfacial layer¹²

$$\rho(y) = \rho_c + \frac{1}{2} (\rho_l - \rho_v) \tanh\left(\frac{y}{2\zeta}\right)$$

with

$$\rho_l = \rho_c + \left(\frac{A}{B} (T_c - T_0)\right)^{\frac{1}{2}}, \quad \rho_v = \rho_c - \left(\frac{A}{B} (T_c - T_0)\right)^{\frac{1}{2}}, \quad \zeta = \left(\frac{C}{2A (T_c - T_0)}\right)^{\frac{1}{2}},$$

where ζ is the characteristic length of the interfacial layer. Moreover, the surface tension of the interfacial layer is :

$$\sigma = \int_{-\infty}^{+\infty} C \rho'^2(y) dy \equiv \frac{\sqrt{C}}{3B} \left(2A(T_c - T_0)\right)^{\frac{3}{2}}$$

3. Weak discontinuity in conservative motions

3.1. Conditions of a weak discontinuity

To the equation of conservative motions given by Eq. (8), we have to add the equation of balance of mass

$$\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \mathbf{u}) = 0, \quad (22)$$

the equation of conservation of the specific entropy $\dot{s} = 0$ and relation (17).

Weak discontinuities of isentropic motions correspond to ρ , s , $\frac{\partial \rho}{\partial \mathbf{x}}$, $\frac{\partial s}{\partial \mathbf{x}}$, continuous through the wave surfaces. As in Hadamard⁹, we denote by $[\]$ the jump of a tensorial quantity through a surface of discontinuity Σ_t . Consequently, with Hadamard's tensorial framework, there exists two Lagrange multipliers λ_1, λ_2 such that :

$$\left[\frac{\partial \rho}{\partial \mathbf{z}} \right] = 0 \Rightarrow \left[\frac{\partial}{\partial \mathbf{z}} \left(\frac{\partial \rho}{\partial \mathbf{z}} \right)^* \right] = \lambda_1 \mathbf{N} \mathbf{N}^* \Rightarrow \left[\frac{\partial}{\partial \mathbf{x}} \left(\frac{\partial \rho}{\partial \mathbf{x}} \right)^* \right] = \lambda_1 \mathbf{n} \mathbf{n}^*, \quad (23a)$$

$$\left[\frac{\partial s}{\partial \mathbf{z}} \right] = 0 \Rightarrow \left[\frac{\partial}{\partial \mathbf{z}} \left(\frac{\partial s}{\partial \mathbf{z}} \right)^* \right] = \lambda_2 \mathbf{N} \mathbf{N}^* \Rightarrow \left[\frac{\partial}{\partial \mathbf{z}} \left(\frac{\partial s}{\partial \mathbf{z}} \right)^* \right] = \lambda_2 \mathbf{n} \mathbf{n}^*, \quad (23b)$$

$$\lambda_1 = [\Delta \rho] \quad \text{and} \quad \lambda_2 = [\Delta s], \quad (23c)$$

From $[\mathbf{V}] = 0$, we deduce $\left[\frac{\partial \mathbf{V}}{\partial \mathbf{z}} \right] = \boldsymbol{\Xi} \mathbf{N}^*$ with $\mathbf{N}^* = (-g, \mathbf{n}^*)$ and $\boldsymbol{\Xi} = \begin{pmatrix} 0 \\ \mathbf{H} \end{pmatrix}$ is a vector Lagrange multiplier, where \mathbf{H} is a 3-vector of D_t . Then,

$$[\dot{\mathbf{u}}] = \left[\frac{\partial \mathbf{V}}{\partial \mathbf{z}} \right] \mathbf{V} = v \mathbf{H}, \quad \text{with} \quad v = \mathbf{N}^* \mathbf{V} \equiv \mathbf{n}^* \mathbf{u} - g$$

Here, v denotes the velocity of the fluid with respect to the wave surface of acceleration Σ_t .

Equation of mass conservation (22) is equivalent to

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

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

$$\mathbf{n}^* \mathbf{H} = 0 \quad (24)$$

Equation of conservation of entropy $\dot{s} = 0$ implies

$$\frac{\partial \dot{s}}{\partial \mathbf{z}} = 0 \Leftrightarrow \frac{\partial}{\partial \mathbf{z}} \left(\frac{\partial s}{\partial \mathbf{z}} \mathbf{V} \right) = 0$$

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 $\frac{\partial}{\partial \mathbf{z}} \left(\frac{\partial s}{\partial \mathbf{z}} \right)^*$ is a symmetric tensor,

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

or,

$$\lambda_2 v + \frac{\partial s}{\partial \mathbf{x}} \mathbf{H} = 0 \quad (25)$$

From Rankine-Hugoniot condition associated to Eq. (9), we obtain the compatibility condition: $[-g \rho \mathbf{u}^* + \rho \mathbf{n}^* \mathbf{u} \mathbf{u}^* - \mathbf{n}^* \sigma] = 0$, and the continuity of $\rho, \rho, \rho, i, s, s, i$, yields $[\text{div } \Phi] = 0$, or

$$[C \Delta \rho + D \Delta s] = 0 \Leftrightarrow C \lambda_1 + D \lambda_2 = 0 \quad (26)$$

Consequently, there exists a scalar Lagrange multiplier λ_3 such that

$$\left[\frac{\partial}{\partial \mathbf{x}} (C \Delta \rho + D \Delta s) \right] = \lambda_3 \mathbf{n}^* \quad (27)$$

Equation of motion (8) yields

$$[\dot{\mathbf{u}}] = [\theta] \text{grad } s - \lambda_3 \mathbf{n},$$

$$\text{or } \rho v \mathbf{H} = -(D \lambda_1 + E \lambda_2) \text{grad } s - \rho \lambda_3 \mathbf{n}$$

By projection on the normal \mathbf{n} to Σ_t and taking relation (24) into account, we obtain

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

By projection on the tangent plane to Σ_t and taking relation (24) into account, we obtain

$$\rho v \mathbf{H} = -(D \lambda_1 + E \lambda_2) \text{grad}_{\text{tg}} s, \quad (28)$$

where $\text{grad}_{\text{tg}} s$ denotes the tangential part of $\text{grad} s$ in Σ_t . Elimination of \mathbf{H} in the relation (28) comes from relation (25), and we get

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

Consequently, we obtain a system of three linear equations with respect to the variables $\lambda_1, \lambda_2, \lambda_3$,

$$\begin{cases} C \lambda_1 + D \lambda_2 = 0, \\ D (\mathbf{n}^* \text{grad} s) \lambda_1 + E (\mathbf{n}^* \text{grad} s) \lambda_2 + \rho \lambda_3 = 0, \\ D (\text{grad}_{\text{tg}} s)^2 \lambda_1 + (E (\text{grad}_{\text{tg}} s)^2 - \rho v^2) \lambda_2 = 0 \end{cases}$$

The compatibility of these three equations yields

$$\rho v^2 = \frac{(CE - D^2)(\text{grad}_{\text{tg}}s)^2}{C} \quad (29)$$

Scalar v is the celerity of the surfaces for isentropic weak discontinuity of acceleration in an isothermal fluid interface near its critical point.

3.2. Celerity of isentropic waves of acceleration

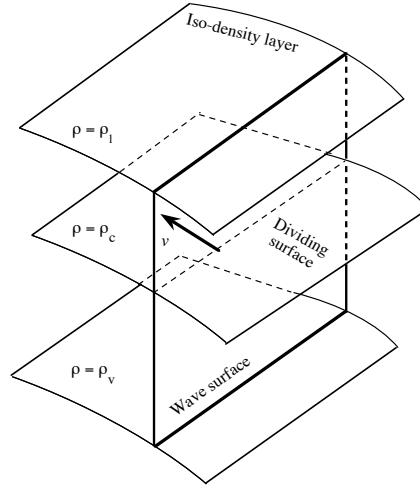


Figure 1. The interfacial layer has a *real thickness* of the order of the characteristic length ζ . The average matter density ρ_c corresponds to a dividing surface, (Rowlinson & Widom, chapter 3). An isentropic wave surface of acceleration is orthogonal to iso-density layers and its celerity of value v is tangential to the dividing surface.

The temperature in liquid and vapor bulks is T_0 . Then, relation (19) yields

$$\text{grad} (A(\rho - \rho_c)^2 + 2\rho s) = 0 \Leftrightarrow A(\rho - \rho_c) \text{grad} \rho + \text{grad} \rho s = 0$$

The value $\rho = \rho_c$ of the matter density in the interface corresponds to the maximum value of $\text{grad} \rho$ (see Eq. (20), when $\mu_c = \mu_1$). The matter density ρ_c is characteristic of the interfacial matter. For such a value, $\text{grad} \rho s = 0$ and $s = (A^2/2B\rho_c)(T_0 - T_c)$. Consequently, $\text{grad} s = \frac{A^2}{2B\rho_c^2}(T_c - T_0) \text{grad} \rho$, and

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

Due to relation (21), we obtain when $\rho = \rho_c$, $C (\text{grad}_{\text{tg}} \rho)^2 = \frac{A^2}{2B} (T_c - T_0)^2$, and consequently,

$$v^2 = \frac{(CE - D^2) A^6 (T_c - T_0)^4}{8 C^2 B^3 \rho_c^5} \quad (30)$$

In the interfacial layer, $\text{grad} \rho$ is normal to iso-density surfaces. The isentropic waves of acceleration associated with a weak discontinuity shear the interfacial layer (see Fig. 1). 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.

4. Results and discussion

Dynamics of liquid-vapor interfaces is easily studied in mechanics by means of second gradient theory which is an extension of the Landau-Ginzburg models in physics. The theory is associated with continuous variations of the matter density through the interfacial layer and was initiated by van der Waals, improved by Rocard in gas theory¹¹ and Cahn and Hilliard in physical chemistry¹. Rowlinson and Widom^{12,19} 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 variations of entropy. Due to the fact the variation of matter density leads the variations of entropy (see Eq. (19)), this extension seems at first sight purely formal and yields the same results that the classical van der Waals model¹⁸ does. Solitary waves, motions in the normal direction to fluid interfaces are not involved in an additive dependance of the entropy gradient. In this paper, we see the dependance of entropy gradient is necessary for isentropic waves of acceleration along the interfaces: the fact 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 by van der Waals, Cahn and Hilliard, Rocard and many others^{10,17,16...} : this kind of waves does not appear when the gradient of entropy is not taken into account. It is easy to see they are exceptional waves in the sense of Lax¹³ 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.

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