" 1st Meeting on Basic constitutive relations for surfaces ". EEC Network "Dynamics of Multiphase Flows across Interfaces". Rapport final de contrat

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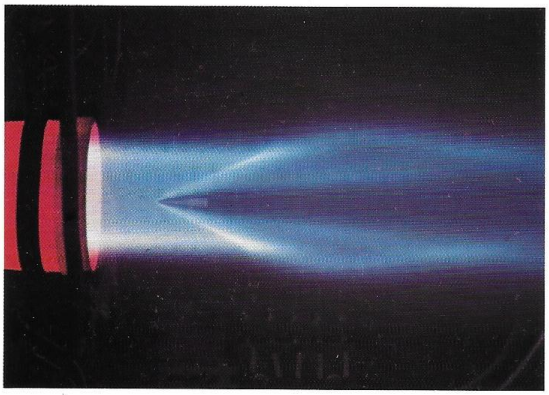

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lst Meeting on

Basic constitutive relations for surfaces

EEC Network “Dynamics of multiphase flows across interfaces”
Contract HCM ERB CHRCT 940481

CNRS Meudon Bellevue
October 14-l5th 1994

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• J. PADDAY
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BALANCE EQUATIONS FOR FLUID CURVILINEAR MEDIA

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Basic equations for fluid curvilinear media

Examples of fluid lines are numerous. Common line between capillary surfaces, some fluid flows along moving and deformable pipes or nozzles, free continuous fluid jets fluid bridges between two attached drops can sometimes be considered as curvilinear fluid media [1, 2, 3].

If we assume that these media verify 3D continuous hypothesis at a small scale, which we will call microscopic (but not molecular) scale, 1D balance equations have to be deduced from 3D balance equations.

The 3D balance equations must be written in an appropriate form permitting easily the transformation into 1D relation. To do this, we have to distinguish firstly the direction (//) which is tangent to the line from the plane ($\perp$) which is normal to this line at a current point.

The classical balance equation for the property F is :

$$\frac{d_v F}{dt} + \Phi_{VF} = P_F \tag{1}$$

where $d_v F/dt$ is the time derivative of the quantity F which is contained in the control volume ($\mathcal{D}$) moving with the local velocity $\vec{V}$, Φ_F is the flux or F through the moving surface ($\partial\mathcal{D}$) of the volume ($\mathcal{D}$) andP_F is the source term.

Using local variables, or excess local quantities, we write :

$$\frac{d_v}{dt}\int_{\mathcal{D}} \rho_F \, d\vartheta + \int_{\partial\mathcal{D}} \vec{J}_{VF} \cdot \vec{n} dS = \int_{\mathcal{D}} p_F \, d\vartheta \tag{2}$$

where ρ_F is the F density (or excess density) per unit volume, $\vec{J}_{VF}$ the local flux density corresponding to the velocity $\vec{V}$ and p_F the production of F per unit volume. The choice between absolute and excess quantities to use in the equations depends on the problem to be solved where some conditions must often be verified to ensure for instance the convergence of integrals of asymptotic analysis.

The classical local form is deduced from (2) :

$$\frac{d_v \rho_F}{dt} + \rho_F \, \vec{\nabla} \cdot \vec{V} + \vec{\nabla} \cdot \vec{J}_{VF} = p_F \tag{3}$$

If we choose the velocity $\vec{V}$ and the derivation operators in an appropriate manner, equation (3) can be written in the form :

$$\frac{d_v \rho_F}{dt} + \rho_F \vec{\nabla}_{//} . \vec{V} + \vec{\nabla}_{\perp} . \vec{J}_{VF} + \vec{\nabla}_{//} . \vec{J}_{VF} = p_F \tag{4}$$

To obtain 1D balance equations along physical fluid lines, it is useful to use particular curvilinear coordinates. It is generally possible to choose orthogonal curvilinear coordinates in such a way that the mean line is a particular line of the system given by fixed values of coordinates x_1 and x_2. Evidently, such a coordinate system is a moving one [4, 5].

We remind hereafter some properties of the transformation between cartesian orthogonal coordinates and such a system. We introduce $\vec{x} = \{x, y, z\}$ and t respectively for the position and the time in the cartesian system and $\vec{\xi} = \{x_1, x_2, x_3\}$ and t for the position and time in the curvilinear system and we have :

$$\vec{x} = \vec{x}\left(\vec{\xi}, t\right) \tag{5}$$

At a given value of t we can define :

$$\vec{h}_i = \frac{\partial \vec{x}}{\partial x_i} \quad , \quad \left|\vec{h}_i\right| = h_i \quad \text{and} \quad \vec{h}_i = h_i \vec{e}_i \tag{6}$$

where $\{\vec{e}_1, \vec{e}_2, \vec{e}_3\}$ form a direct orthogonal basis.

We can also define X_i :

$$dX_i = h_i \, dx_i \tag{7}$$

So, for a curve $(\mathcal{C}_i)$ obtained by fixing the values of x_j and x_k $(j \neq k \neq i = 1, 2, 3)$, the curvature vector $\vec{\mathcal{C}}_i$ is the following :

$$\vec{\mathcal{C}}_i = \frac{\partial \vec{e}_i}{\partial X_i} = \frac{1}{h_i} \frac{\partial \vec{e}_i}{\partial x_i} = - \frac{1}{h_i} \left(\frac{h_{i,j}}{h_j} \vec{e}_j + \frac{h_{i,k}}{h_k} \vec{e}_k \right) \tag{8}$$

and for a surface (S_i), obtained for a given value of x_i, the mean curvature C_i if the following :

$$C_i = \frac{1}{h_i} \left(\frac{h_{i,j}}{h_j} + \frac{h_{k,i}}{h_k} \right) . \tag{9}$$

For a given velocity field $\vec{V}(\vec{x}, t)$, written in curvilinear coordinates as $\vec{V}(\vec{\xi}, t)$, we can define : the line stretch of curve $(\mathcal{C}_3)$ as :

$$\frac{1}{dX_3}\frac{d(dX_3)}{dt} = \frac{1}{h_3}\left(V_{3,3} + V_1\frac{h_{3,1}}{h_1} + V_2\frac{h_{3,2}}{h_2}\right) , \tag{10}$$

and the same for $(\mathcal{C}_1)$ and $(\mathcal{C}_2)$, the surface stretch of surface (S_3) as :

$$\frac{1}{dS_3}\frac{d(dS_3)}{dt} = \frac{1}{dX_1}\frac{d(dX_1)}{dt} + \frac{1}{dX_2}\frac{d(dX_2)}{dt} \tag{11}$$

and the volume expansion :

$$\frac{1}{d\vartheta}\frac{d(d\vartheta)}{dt} = \sum_{i=1}^{3}\frac{1}{dX_i}\frac{d(dX_i)}{dt} = \vec{\nabla} \cdot \vec{V} \tag{12}$$

If we suppose that :

- the velocity $\vec{V}$ and in particular its component $\vec{V}_\perp$ normal to the line, varies very slightly through the thickness of this line that is that along the surface S3 : $V_{1,1} = V_{2,2} \equiv 0$,

- the curvature of (S_3) is negligible : $C_3 << 1/L$, where L is a reference hydrodynamic length,

- the curves $(\mathcal{C}_1)$ and $(\mathcal{C}_2)$ have also small curvatures $\vec{e}_2 \cdot \vec{C}_1$ and $\vec{e}_1 \cdot \vec{C}_2$, then, we can put :

$$\rho_F^l = \int_{S_3} \rho_F \, dS \quad , \quad \vec{J}_{VF}^{\,l} = \int_{S_3} \vec{J}_{VF} \, dS \quad , \quad p_F^l = \int_{S_3} p_F \, dS \, . \tag{13}$$

and we obtain the line balance equation of the property F :

$$\frac{d_v \rho_F^l}{dt} + \rho_F^l \, \vec{\nabla}_{//} \cdot \vec{V} + \varphi_{VF}^l + \vec{\nabla}_{//} \cdot \vec{J}_{VF}^{\,l} = p_F^l \tag{14}$$

with :

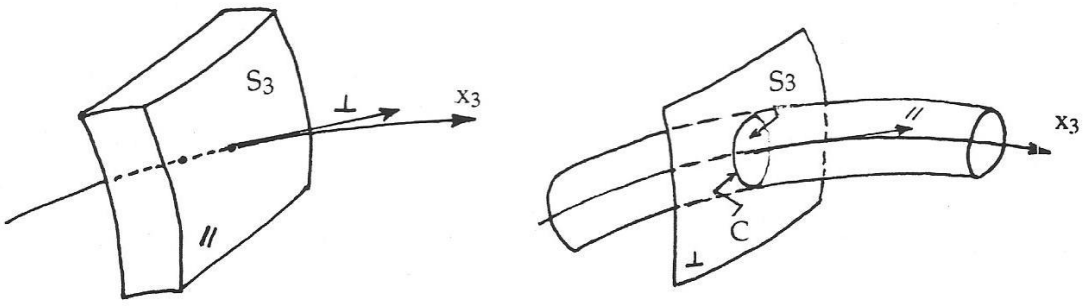
(15)
$$\begin{cases} \varphi^{1}_{VF} = \int_S \vec{\nabla}_\perp \cdot \vec{J}_{VF}\, dS = \int_c \vec{J}_{VF\perp} \cdot \vec{n}\, dc \quad \text{(peripheric term, see Fig. 1)} \\ \vec{\nabla}_{//} \cdot \vec{J}^{1}_{VF} = \dfrac{\partial \vec{J}^{1}_{VF//}}{\partial s} + \vec{J}^{1}_{VF\perp} \cdot \vec{e}_3 \ , \quad ds = dX_3 = h_3\, dx_3 \\ \vec{\nabla}_{//} \cdot \vec{V} = \dfrac{\partial V_{//}}{\partial s} + \vec{V}_\perp \cdot \vec{e}_3 \ , \quad \text{stretch given by eq. 10.} \end{cases}$$

Comparison with the case of a fluid interface

We can remark here that the equation (14) has been obtained in the same manner as an interface balance equation. In this last case, we start from an equation analogous to (4) with the difference that the direction ($\perp$) is normal to the interface and that ($//$) is tangential to the interface. We obtain by integration along the direction x_3 normal to the interface :

(16)
$$\frac{d_v \rho^{S}_F}{dt} + \rho^{S}_F \vec{\nabla}_{//} \cdot \vec{V} + [J_{VF\perp}] + \vec{\nabla}_{//} \cdot \vec{J}^{S}_{VF} = p^{S}_F \ .$$

(see Fig. 1), $\vec{\nabla}_{//} \cdot \vec{V}$ being the stretch given by eq. 11.



Interface Line

Figure 1

The hypotheses are similar : one can construct a mixed velocity vector $\vec{V}$ which presents very small variations at the crossing of the interface whose thickness does not vary locally (for a line, it does not vary crossing the line in the surface S_3) and the procedure is analogous :

- writing the (excess) 3D balance equations in a system of varying curvilinear coordinates
- integrating along the x_3 coordinate (on the surface S_3 for a line).

Application to a pipe flow

We suppose that the pipe has its proper deformation and that the fluid has a uniform velocity in a cross section (S_3) except through a thin boundary layer near the wall. The effect of this layer is characterized by a friction force p_f per unit length (Fig. 2).

We obtain the mass balance equation :

$$\frac{d_v \rho^l}{dt} + \rho^l \vec{\nabla}_{//} . \vec{V} = 0 \quad , \quad \rho^l_M = \rho^l \tag{17}$$

and the momentum balance equation

$$\frac{d_v \vec{\rho}_I^{\,l}}{dt} + \vec{\rho}_I^{\,l} \vec{\nabla}_{//} . \vec{V} + \vec{p}_\perp + p_f \vec{e}_3 + \vec{\nabla}_{//} p^l = \rho^l \left(\vec{g} - \vec{\gamma}_e - \vec{\gamma}_c\right) \tag{18}$$

where $\vec{\rho}_I^{\,l}$ is the line momentum, $\vec{p}_\perp$ is a line force acting normally to the pipe. This force is counterbalanced in particular by the centrifugal force appearing in the acceleration term $\frac{d_v \vec{\rho}_I^{\,l}}{dt}$. The term p^l is a line pressure ($(- p^l)$ is a line tension) and the right-hand term contains gravity and inertial forces.

We have for the peripheric force $\vec{p}_\perp + p_f \vec{e}_3 = \vec{\varphi}_{VI}^{\,l}$

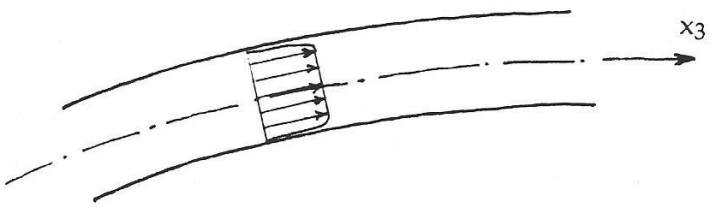


Figure 2

Application to Euler's first law common line

J.C. Slattery [5] writes the impulsion balance equation for the common line between three capillary surfaces. In this case, the peripheric force $\vec{\varphi}_{VI}^{\,l}$ results from the actions of the capillary surfaces.

If we neglect the mass transfer at the common line and if we neglect the effect of inertial forces on the common line, the momentum balance on the common line may be expressed in terms of surface tension (Fig. 3) :

(19) $$\gamma^{(AB)}\,\vec{\nu}^{(AB)} + \gamma^{(AS)}\,\vec{\nu}^{(AS)} + \gamma^{(BS)}\,\vec{\nu}^{(BS)} = 0 \ ,$$

where $\vec{\nu}^{(AB)}$, $\vec{\nu}^{(AS)}$ and $\vec{\nu}^{(BS)}$ are the unit vectors that are normal to the common line and that are both tangent to and directed into the A-B, A-S and B-S dividing surfaces respectively.

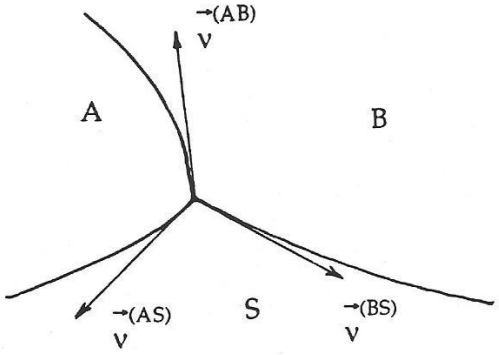


Figure 3

The problem of constitutive relations

We have given a general procedure for obtaining balance equations for fluid curvilinear media. A more detailed analysis have to be made in each case to establish the governing equations for mass, species, momentum and energy in the adequate form. In addition, it is necessary, before solving the system, to close it with constitutive relations. Some of them can be obtained from 3D constitutive relations by simple integration. But the problem is not always easy to solve for several reasons. Two of them are the following :

- 3D constitutive relations are often themselves unknown,
- when we know such 3D constitutive relations, they are generally nonlinear and thus difficult to treat for 3D-2D or 3D-1D mathematical transition.

This paper has been partly written in relation with a research presently developed in the "Direction Scientifique de l'Energétique" of ONERA.

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VERS UNE THERMODYNAMIQUE HORS D'ÉQUILIBRE NON LINÉAIRE

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La théorie du second gradient appliquée aux interfaces : Modèles de mécanique des milieux continus dans les interfaces fluides

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La théorie du second gradient pour les fluides permet de prendre en compte les systèmes dans lesquels interviennent des interfaces fluides. La capillarité interne en est un cas particulier simple.
On peut ainsi proposer par des analyses limites le comportement des interfaces entre phases fluides dans le cas où ces interfaces sont de faible épaisseur et alors considérées comme des surfaces matérielles.
Une telle théorie permet de calculer la tension superficielle aussi bien dans le cas des interfaces minces que pour des interfaces épaisses. Elle permet d'obtenir le rayon de nucléation des bulles ou des gouttes microscopiques et d'étendre ainsi des théories macroscopiques du type Laplace. La stabilité des interfaces peut être appréhendée par des équations différentielles ou aux dérivées partielles.
Le modèle des milieux continus proposé s'étend à la dynamique. Les équations conduisent à la définition d'un tenseur des contraintes. Pour les fluides, la théorie du second gradient ne conduit pas à un tenseur des contraintes isotrope. Les forces de contact sont d'une nature complètement différente de celle d'un milieu de Cauchy. Les conditions classiques des coupures de Cauchy ne sont en effet pas adaptées pour étudier le comportement non linéaire des fluides doués de capillarité interne. On obtient ainsi des forces de contact concentrées sur les lignes frontières associées aux surfaces "coupures de Cauchy".
De telles conditions sont indispensables par exemple pour étudier la stabilité des films minces en contact avec des parois solides.
Dans les régions interfaciales, la théorie de la capillarité interne, différente de celle des milieux continus classiques, est en accord avec des modèles moléculaires du type "champ moyen". Elle permet en particulier d'étudier la dynamique au voisinage des points critiques (les interfaces deviennent macroscopiques), mais surtout elle autorise une modélisation -certes qualitative- mais avantageuse, de la dynamique des changements de phases entre milieux fluides ou mélanges de fluides.

1 - Les equations du mouvement et de la thermodynamique des fluides doués de capillarité interne

L' équation du mouvement est celle donnée classiquement dans la littérature avec des termes supplémentaires du type second gradient.
Nous supposerons dans cette approche que seuls les gradients du premier ordre en densité interviennent dans l'énergie interne spécifique

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

Dans une phase homogène où les gradients sont nuls, l'énergie est alors:

$$\varepsilon = f(\rho,s,0) = \alpha(\rho,s)$$

En pratique, nous prendrons la forme

$$\varepsilon = \alpha + Q/(2\rho) \quad \text{où} \quad Q = C\,(\text{grad}\,\rho)^2$$

Le modèle le plus simple permettant de tenir compte de la masse volumique et de son gradient fait intervenir *une unique grandeur physique supplémentaire* C *constante de capillarité interne.* Dans des unités usuelles, sa valeur est faible et elle n'intervient effectivement que dans les interfaces. L'équation du mouvement s'écrit:

$$\rho\,\Gamma + \text{grad}\,P + \rho\,\text{grad}\,(\,\Omega - C\,\Delta\rho\,) - \text{div}\,\sigma_V = 0$$

où P note la pression de van der Waals ou celle associée à des modèles comparables, Ω représente le potentiel des forces de masse, σ_V est le tenseur des contraintes visqueuses, Γ est l'accélération du fluide. Pour un fluide non visqueux et un écoulement isotherme, l'équation du mouvement devient:

$$\Gamma + \text{grad}(\mu - C\,\Delta\rho + \Omega\,) = 0$$

où μ note l'enthalpie libre spécifique ou potentiel chimique du fluide.

Si nous nous contentons de forces dissipatives du type Navier-Stokes et non pas, comme il serait logique ici, de forces faisant intervenir des termes de gradients plus élevés- nous aurons à ajouter dans l'équation de l'énergie un vecteur $\sigma_V V$. On conservera les termes habituels de flux de chaleur et de rayonnement (q et r).

$$\partial e/\partial t + \text{div}\,[(e+P)V] - \text{div}\,W - \text{div}\,(\sigma_V V) + \text{div}\,q - r = \rho\,\partial\Omega/\partial t$$

où $e = \rho(1/2\ V^2 + \varepsilon + \Omega)$ et l'équation de l'énergie comporte un terme de flux d'énergie $W = C\,(d\rho/dt)\ \text{grad}\,\rho$.
L'équation de la température devient:

$$\rho\,T\,ds/dt + \text{div}\,q - r - \Psi = 0$$

où Ψ est la fonction de dissipation et T la température Kelvin.

Nous exprimerons le second principe de la thermodynamique en écrivant $\Psi \geq 0$
ce qui donne l'inégalité de Planck:

$$\rho\,T\,ds/dt + \text{div}\,q - r \geq O$$

On constate que cette inégalité est formellement inchangée. Si on ajoute une loi de Fourier sous la forme

$$q\ .\ \text{grad}\,T \leq 0$$

on retrouve formellement l'inégalité de Clausius-Duhem :

$$\rho\,(ds/dt) + \text{div}(q/T) - r/T \geq 0.$$

2 - Conditions aux limites pour les fluides doués de capillarité interne

Le principe des travaux virtuels appliqué à des milieux doués de capillarité interne nous permet d'obtenir les conditions aux limites. A la différence des milieux élastiques, nous obtenons des conditions différentes des conditions de coupures de Cauchy sur le bord du milieu continu. Elles font intervenir la normale mais aussi la courbure du bord. On obtient ainsi des forces de contact concentrées sur les lignes frontières.
Sur le bord (S_t) du milieu continu, on obtient:

$$\rho\,u\,V + [\,P\ - C/2\,(\text{grad}\,\rho)^2 - C\,\rho\Delta\rho + C\,(\text{grad}\,\rho)\,(\text{grad}\,\rho)^t - 2A/R_m]\,n - \text{grad}_{tg}\,A = P$$

$$- u\,e_1 - [\,P\ - 2A/R_m]\,n^t\,V - n^t\ \partial(AV)/\partial x\,n + \text{div}\,(AV) + C\,\partial\rho/\partial t\,\text{grad}\,\rho = \kappa$$

$$- A\,n^t\,V = \lambda \quad \text{et} \quad A = S$$

où $A = C\rho\ d\rho/dn$, n désigne la normale à (S_t), R_m le rayon de courbure moyen, u la vitesse du fluide à travers (S_t), e_1 l'énergie libre du fluide, P, κ, λ et S les termes équilibrant les efforts du fluide sur la surface.

Nous obtenons sur les arêtes (Γ_t) de (S_t) les conditions supplémentaires:

$$A\,n' = R \quad \text{et} \quad A\,n'\,V = \mu$$

où n' désigne le vecteur unitaire $t \times n$ où t est le vecteur unitaire tangent à (Γ_t) et R et les termes équilibrant les efforts du fluide capillaire sur les arêtes.

Il est maintenant important de montrer qu'une telle théorie des milieux continus, compatible avec les théories moléculaires dites du champ moyen, permet de représenter commodément les interfaces fluides en équilibre ou en mouvement: c'est l'objet des trois paragraphes qui suivent:

3 - Calcul de la tension superficielle d'une interface courbe ou plane

Les surfaces d'égale densité matérialisant l'interface sont considérées comme des surfaces parallèles. Elles déterminent un système de coordonnées orthogonales. Les notations sont celles donnés classiquement. L'indice 3 est relatif à la direction normale aux surfaces d'égale densité pour le sens des densités croissantes.
En négligeant les forces de masse, la composante de l'équation de la quantité de mouvement normale à l'interface considérée dans le cas de l'équilibre s'écrit:

$$(1/h_3)(\partial P/\partial x_3) = C\,\rho\,(1/h_3)\,(\partial\Delta\rho/\partial x_3)$$

Nous tenons compte des ordres de grandeur linéique de l'interface et nous ne considérons pas le cas des bulles et des gouttes de la dimension de quelques rayons moléculaires. Nous effectuons une analyse limite où l'on suppose que le paramètre relatif à l'épaisseur de la couche capillaire tend vers zéro. L'intégration de l'équation précédente sur la troisième ligne coordonnée (normale à l'interface) nous donne:

$$P - P_v = C\,\rho\,\Delta\rho - C \int_{x_{3,v}}^{x_{3,l}} \Delta\rho\,(\partial\rho/\partial x_3)\,dx_3$$

R_m représentant le rayon de courbure moyen des surfaces d'égale densité. On en déduit:

$$P - P_v = C\,[\,\rho\,\Delta\rho - 1/2\,(\text{grad}\,\rho)^2] + 2C/R_m \int_{x_{3,v}}^{x_{3,l}} (\text{grad}\,\rho)^2\,h_3\,dx_3$$

En notant $dn = h_3\,dx_3$, on obtient:

$$P_l - P_v = 2\,\sigma/R_m \qquad \text{où} \qquad \sigma = C \int_{n_v}^{n_l} (\text{grad}\,\rho)^2\,dn,$$

expression de la formule de Laplace pour des interfaces courbes. σ s'interprète comme la tension superficielle du fluide que nous rencontrons dans le cas des interfaces planes.

4- Etude des bulles (ou gouttes) microscopiques

Dès 1948, Tolman s'est préoccupé d'étudier la tension superficielle des bulles en fonction de leur rayon. Des mesures expérimentales ont été faites pour des bulles de la dimension de quelques rayons moléculaires. A l'aide du modèle de capillarité interne, nous comparons l'énergie libre d'un fluide homogène de densité ρ_0 contenu dans un domaine D à l'énergie libre de la même masse contenant une petite bulle V. Cela nous conduit à des expressions d'énergie de nucléation respectivement en théorie de Laplace et en théorie du second gradient:

$$W = 4\,\pi\,R\,\sigma + 4/3\,R^3\,[\,\psi(\rho_v) - \psi(\rho_l) + \mu(\rho_l)(\,\rho_l - \rho_v\,)] \quad \text{(Laplace)}$$

$$W = \int_{R^3} [\,\psi(\rho) - \psi(\rho_l) + \mu(\rho_l)(\,\rho_l - \rho\,) + C/2\,(\text{grad}\,\rho)^2\,] \quad \text{(Théorie du second gradient)}$$

où ψ représente l'énergie libre volumique du fluide homogène.
L'équation différentielle donnant l'équilibre en coordonnées sphériques est:

$$C\,d^2\rho/dr^2 + 2\,C/r\,d\rho/dr = \mu(\rho) - \mu(\rho_l)$$

nous permettent de proposer un rayon R et une tension superficielle σ pour la bulle microscopique dans le cas où la théorie de Laplace n'est plus valable:

$$R = [\,2C \int_0^\infty r^2\,\rho'^2]^{1/3}\,[\,\psi(\rho_l) - \psi(\rho_v) + \mu(\rho_l)(\,\rho_v - \rho_l\,)]^{-1/3}$$

$$\sigma = [\,C/4 \int_0^\infty r^2\,\rho'^2]^{1/3}\,[\,\psi(\rho_l) - \psi(\rho_v) + \mu(\rho_l)(\,\rho_v - \rho_l\,)]^{2/3}$$

Ces expressions nécessitent des lois d'état non-convexe (type van der Waals). Des expériences numériques ont été menées; elles montrent que, pour des bulles de rayon voisin du rayon critique, la variation prévue de la tension superficielle correspond aux mesures expérimentales (par exemple de Fisher).

5- Ondes au voisinage du point critique d'un fluide

La théorie des ondes voyageuses de transitions de phases représente vitesse et densité sous la forme:

$$V = V(X - q\,t) \quad \text{et} \quad \rho = \rho(X - q\,t)$$

où $q \in \mathbb{R}$ note la célérité de l'onde dans l'espace de référence. Posons $\zeta = X - q\,t$. L'équation du mouvement non visqueux devient l'équation des ondes unidimensionnelles

$$C\,\frac{d^2\rho}{dx^2} = \mu - \mu_o + \frac{q^2}{2\rho^2} + \Omega$$

où μ_o est une constante d'intégration. Au voisinage du point critique, le potentiel chimique d'un fluide à un seul constituant est de la forme:

$$\mu = \mu^c - \mu^c_{o1}\,\Delta T - \mu^c_{11}\,\Delta\rho\,\Delta T + \frac{1}{6}\,\mu^c_{3o}\,(\Delta\rho)^3$$

où $\Delta\rho = \rho - \rho_c$ et $\Delta T = T_c - T$ notent les écarts du champ de masse volumique et de la température relativement à leur valeur au point critique. Les coefficients sont les valeurs au point critique de dérivées partielles de μ. Dans le cas unidimensionnel isotherme, l'équation des ondes devient en négligeant les forces dues à la pesanteur:

$$C\,\frac{d^2\rho}{dx^2} = -A\,\Delta\rho\,\Delta T + B\,(\Delta\rho)^3 + \frac{q^2}{2\rho^2} + a_o$$

où $A = \mu^c_{11}$ et $B = \frac{1}{6}\,\mu^c_{3o}$ et a_o est une constante d'intégration.

Puisque nous sommes proche de la température critique, $c = \frac{q}{\rho_c}$ représente *la vitesse de l'onde* dans l'espace physique.

La théorie du champ moyen nous permet à l'aide de la mécanique des milieux continus d'envisager l'existence d'ondes solitaires au voisinage du point critique. Nous avons obtenu
- soit des ondes de la forme des interfaces liquide-vapeur ayant au dessous de la température critique une énergie de tension superficielle supérieure à celle correspondant à l'équilibre
- soit des ondes de matière qui ne peuvent exister à l'équilibre.

Au dessus de la température critique le fluide se comporte comme un milieu élastique, les ondes sont supersoniques. La célérité des ondes dépend de l'écart de température avec sa valeur critique. Au dessous de la température critique le fluide se comporte comme un milieu sans rigidité, la célérité de l'onde étant arbitraire.

Il serait maintenant important que les calculs des vitesses d'onde puissent être comparés favorablement (ou même défavorablement) à des résultats d'expériences pour différents fluides. Il serait en outre intéressant de faire intervenir la viscosité dans l'étude des mouvements au voisinage du point critique.

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MODELISATION ASYMPTOTIQUE DES INTERFACES FLUIDE-FLUIDE

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1. INTRODUCTION

Notre but est de discuter les conditions locales de saut pour un système de deux fluides (fluide + et fluide -) séparés par une interface de forme arbitraire et en mouvement. Nous considérerons la région interfaciale entre les deux fluides, d'une part comme une surface moyenne de séparation entre les deux fluides que nous appellerons "interface" (aspect macroscopique) et d'autre part comme une zone de transition à travers laquelle les variations des paramètres physiques sont grandes que nous appellerons "couche interfaciale" (aspect microscopique). Cette couche interfaciale, ou encore zone capillaire, est considérée comme un milieu tridimensionnel, fluide, avec un ou plusieurs constituants. Caractérisée par le présence de forts gradients de densité, il est naturel d'imaginer que l'excès d'énergie interne de l'interface leur est dû.

La modélisation asymptotique consiste à considérer que la couche interfaciale est d'épaisseur δ très petite devant le rayon de courbure R des surfaces isodensités situées dans son intérieur. Dans cette approche (δ / R $\rightarrow$ 0), la couche est vue comme une surface de discontinuité. Les lois usuelles de saut à travers une interface sont trouvées.

De très nombreux travaux portent sur l'écriture des conditions de saut à travers une interface fluide-fluide. Une approche souvent utilisée consiste à considérer l'interface comme une surface de discontinuité possédant des propriétés matérielles, celles-ci étant introduites par analogie avec le cas tridimensionnel [1 à 3]. Dans la plus part des applications, il suffit en effet de retenir une modélisation par une surface de discontinuité sans masse mais possédant une énergie interne par unité d'aire reliée au phénomène de tension superficielle. Mais pour décrire certains comportements (viscosités au niveau de l'interface, voisinage du point critique, ...) il est nécessaire d'avoir une modélisation moins grossière. L'approche asymptotique que nous proposons est un essai pour une meilleure modélisation.

2. QUANTITES INTERFACIALES ET LOIS DE CONSERVATION

La couche interfaciale entre les deux fluides est une fine zone de transition et on introduit une surface géométrique S à l'intérieur de cette zone. On note $\bar{n}$ le vecteur unitaire normal à S dirigé du fluide - vers le fluide + (figure 1). Les frontières de la couche sont définies asymptotiquement et sont à la distance ξ_+ et ξ_- de la surface S. Suivant les travaux de Ishii [6], nous introduisons la masse interfaciale ρ_a par unité d'aire et la vitesse moyenne $\bar{V}_s$ des particules au sein de la couche :

$$\rho_a = \int_{\xi_-}^{\xi_+} \rho \, d\xi \qquad \rho_a \vec{V}_s = \int_{\xi_-}^{\xi_+} \rho \vec{V} \, d\xi \tag{1}$$

La vitesse $\vec{V}_s$ apparaît comme une vitesse barycentrique. Cette vitesse est différente de la vitesse géométrique $\vec{W}$ de déplacement de l'interface S (dont seule la composante normale est bien définie): plus précisément les composantes normales de $\vec{V}_s$ et de $\vec{W}$ sont différentes. Cette différence conduit notamment à l'introduction d'un terme supplémentaire dans la production d'entropie interfaciale comme on le verra plus loin.

Les grandeurs matérielles attachées à l'interface sont toutes définies à partir d'une intégration sur l'épaisseur de la couche. Une quantité physique quelconque ψ définie dans tout l'espace possède en général un fort gradient à l'intérieur de la couche avec les valeurs asymptotiques ψ_- et ψ_+ sur les frontières de la couche. Nous posons:

$$\psi_a = \rho_a \psi_s = \int_{\xi_-}^{\xi_+} \rho \, \psi \, d\xi \quad . \tag{2}$$

Remarquons que ψ_a est une quantité définie par unité d'aire et ψ_s une quantité définie par unité de masse interfaciale. Ces définitions étant posées, nous écrivons classiquement, pour une quantité $\rho\psi$ définie par unité de volume, l'équation de conservation dans un fin volume $\mathscr{V}$ matériel qui contient la couche de transition. Ce volume $\mathscr{V}$ coupe perpendiculairement la surface S suivant un morceau de surface $\mathscr{A}$ de contour $\mathscr{C}$ (figure 2), la surface S se déplaçant avec la vitesse $\vec{W}$:

$$\frac{d}{dt} \int_{\mathscr{V}} \rho\psi \, dv = \int_{\partial\mathscr{V}} \vec{J} . \vec{n} \, dS + \int_{\mathscr{V}} \rho\Phi \, dv \quad . \tag{3}$$

Ici, $\vec{J}$ désigne le vecteur flux associé à la quantité $\rho\psi$ et $\rho\Phi$ le taux de densité volumique de ce qui est fourni par l'extérieur. Sachant que δ / R est très petit, et moyennant certaines approximations [4, 5, 7], nous aboutissons à l'équation de bilan interfacial sous forme locale:

$$\frac{\delta_s}{\delta t}(\rho_a \psi_s) + \rho_a \psi_s \vec{\nabla}_s . \vec{W} = \left[\rho\psi\left(\vec{V} - \vec{W}\right) + \vec{J}\right] . \vec{n} - \vec{\nabla}_s . \vec{J}_{a//} + \rho_a \Phi_s \tag{4}$$

avec:

$$\vec{J}_a = \int_{\xi_-}^{\xi_+} \left\{\rho\psi\left(\vec{V} - \vec{V}_s\right) + \vec{J}\right\} d\xi \quad . \tag{5}$$

Dans (4), le crochet [ ] est mis pour la différence des valeurs asymptotiques + et - de la grandeur figurant dans son intérieur. L'expression donnée pour $\vec{J}_a$, où figure la vitesse moyenne $\vec{V}_s$, tient compte du fait que nous avons introduit une composante tangentielle $\vec{W}_{//}$ pour la vitesse de déplacement de S de telle sorte que: $\vec{W} = \vec{W}_{//} + \vec{W}_{\perp} = \vec{V}_{s//} + \vec{W}_{\perp}$. La dérivée par rapport au temps est la dérivée convective associée à la vitesse $\vec{W}$ et prise sur la surface; la notation $\vec{\nabla}_s .$ représente la divergence surfacique et $\rho_a \Phi_s$ est le taux de densité surfacique de ce qui est fourni par l'extérieur. Nous remarquons que seule la composante tangentielle $\vec{J}_{a//}$ de $\vec{J}_a$ est présente; de plus, de par sa définition, ce vecteur flux $\vec{J}_{a//}$ contient deux contribution: l'une correspond à l'agitation tangentielle des particules fluides dans la couche, et l'autre à la valeur moyenne de $\vec{J}_{//}$ à travers la couche.

Les équations locales de saut relatives à la conservation de la masse, de la quantité de mouvement et de l'énergie sont aisées à écrire en prenant pour $\rho\psi$ la masse volumique ρ, la quantité de mouvement $\rho\vec{V}$ et l'énergie $\rho\left(e + (1/2)\vec{V}^2\right)$, e étant l'énergie interne par unité de volume [4, 5, 7].

3. PRODUCTION D'ENTROPIE INTERFACIALE

Par une démarche analogue à celle utilisée pour obtenir les conditions locales de saut, on peut, à partir de l'inégalité d'entropie écrite pour le milieu tridimensionnel,, déduire une inégalité pour l'entropie interfaciale:

$$\rho_a \frac{\delta_s}{\delta t}(s_s) = \left[\dot{m}(s - s_s) + \frac{\vec{q}.\vec{n}}{T}\right] + \vec{\nabla}_s.\frac{\vec{q}_a}{T_s} - \frac{r_a}{T_s} \geq 0 \quad . \tag{6}$$

L'entropie interfaciale s_s est définie par une formule similaire à (2), et pour la température T_s de l'interface, nous avons été conduits à poser:

$$\frac{\rho_a}{T_s} = \int_{\xi_-}^{\xi_+} \frac{\rho}{T}\, d\xi \quad . \tag{7}$$

Dans (6), $\dot{m}_\pm$ est la perte du fluide $\pm$ à travers S par unités de temps et d'aire, $\vec{q}_\pm$ est le vecteur flux de chaleur dans le fluide $\pm$ et $\vec{q}_a$ le vecteur flux de chaleur interfacial.

Enfin, en adoptant la relation classique de Gibbs: $de_s = T_s\, ds_s + \gamma\, d(1/\rho_a)$, où γ désigne la tension superficielle, nous obtenons l'expression suivante pour la production d'entropie interfaciale:

$$\begin{aligned}\Delta = \frac{1}{T_s}\Bigg\{\Bigg[\dot{m}\Big(g - g_s + (T - T_s)s + \frac{1}{2}\left(\vec{V} - \vec{V}_s\right)^2\Big) + \vec{q}.\vec{n}\,\frac{T - T_s}{T} - \vec{\vec{\tau}}:\left(\vec{V} - \vec{V}_s\right)\vec{n}\Bigg] \\ + \vec{\vec{\tau}}_{a//}:\vec{V}_s\vec{V}_s - \vec{q}_{a//}.\frac{\vec{V}_s T_s}{T_s} + \left(p_+ - p_- + \gamma\,\vec{\nabla}.\vec{n}\right)\left(\vec{V}_s - \vec{W}\right).\vec{n}\Bigg\} \geq 0\end{aligned} \tag{8}$$

L'enthalpie libre $g_\pm$ du fluide $\pm$ et celle g_s de l'interface ont été introduites, de même que les tenseurs des contraintes visqueuses $\vec{\vec{\tau}}_\pm$ et $\vec{\vec{\tau}}_{a//}$ (les fluides à l'extérieur de la couche interfaciale sont supposés newtoniens).

Le dernier terme dans la production d'entropie Δ n'est pas usuel. Il prend en compte le désaccord entre les composantes normales de la vitesse matérielle $\vec{V}_s$ et de la vitesse de déplacement de l'interface $\vec{W}$. Il faut remarquer que le premier facteur $\left(p_+ - p_- + \gamma\,\vec{\nabla}.\vec{n}\right)$ donne, quand on l'annule, l'équation classique de Laplace pour une interface en équilibre.

4. CONCLUSION

Le milieu tridimensionnel constituant la couche interfaciale n'est pas un fluide newtonien. L'utilisation du principe des puissances virtuelles dans le cadre d'une théorie du second gradient permet de faire une description des efforts intérieurs. En particulier le tenseur des contraintes en situation non dissipative est non sphérique [7].

Le cas limite où la masse interfaciale ρ_a est nulle est intéressant. L'énergie interne interfaciale e_a et l'entropie interfaciale s_a par unité d'aire demeurent finies. Dans les conditions locales de saut obtenues par passage à la limite, la vitesse normale $\vec{V}_{s\perp}$ n'apparaît plus. Seules les vitesses $\vec{V}_{s//}$ et $\vec{W}_{\perp}$ sont présentes. La distinction entre $\vec{V}_{s\perp}$ et $\vec{W}_{\perp}$ n'est plus à considérer. Les lois usuelles de saut à travers une interface sans masse sont retrouvées.

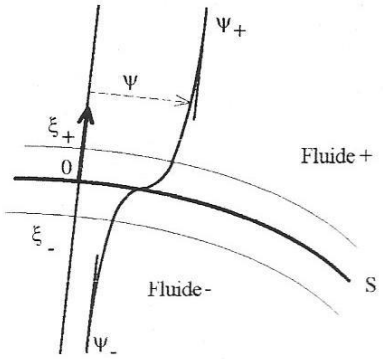

Figure 1

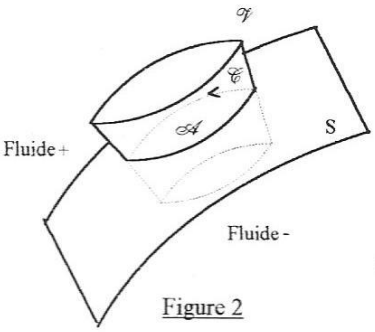

Figure 2

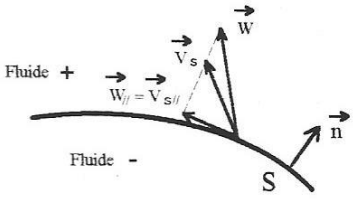

Figure 3

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The authors wish to dedicate the present paper to the memory of F.C.Goodrich

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Surface excess momentum balances by integration across the surface of the volume balances.

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Introduction.

After the first unpublished attempts made by the authors in 1972, F.C. Goodrich [1] during his stay in Sanfeld's group published a paper on surface viscosities in which he established the basis for the understanding of surface transport properties in terms of "excess " quantities. He started from the concept of Gibbs attributing to the dividing surface a content of matter as well as a content of energy and of entropy and generalized this description to the transport coefficients. In the gibbsian method, any extensive property Q of a two phase system may be split into three terms

$$Q = Q^1 + Q^2 + q \qquad (1)$$

in which q is the contribution of the interface, Q^1 and Q^2 being the contribution of the bulk phases. It is evident that the sum $Q^1 + Q^2 + q$ is invariant, but that the individual values of the terms depends upon the location of the dividing surface. An important simplification already introduced by Gibbs [2]was the definition of "relative excess surface quantities" which are independant of the location of the dividing surface. These relative excess surface quantities are chosen as the excess quantities for which the absolute surface excess of one of the components is taken equal to zero. In the gibbsian approach, the adsorbed mass of the solvant in a multicomponent system was chosen as being zero to define the relative adsorptions $\Gamma_{\gamma 1}$ of the other components as well as for defining the relative surface internal energy $u^a{}_1$ or entropy $s^a{}_1$. The relation defining these relative quantities is

$$\Gamma_{\gamma 1} = \Gamma_{\gamma}^{a} - \Gamma_{1}^{a} \frac{C_{\gamma}^{'} - C_{\gamma}^{''}}{C_{1}^{'} - C_{1}^{''}}$$

$$u_{1}^{a} = u^{a} - \Gamma_{1}^{a} \frac{u^{'} - u^{''}}{C_{1}^{'} - C_{1}^{''}}$$

$$s_{1}^{a} = s^{a} - \Gamma_{1}^{a} \frac{s^{'} - s^{''}}{C_{1}^{'} - C_{1}^{''}} \qquad (2)$$

where Γ_{γ}^{a} is the absolute surface excess of γ, Γ_{1}^{a} is the absolute excess of the solvant 1, u^{a} is the absolute excess surface internal energy , u_{1}^{a} is the relative excess surface internal energy, s^{a} is the absolute excess surface entropy, s_{1}^{a} is the relative excess surface entropy, $C_{\gamma}^{'}$ and $C_{\gamma}^{''}$ are the mean concentrations of γ in the two bulk phases, $C_{1}^{'}$ and $C_{1}^{''}$ the mean concentrations of the solvant 1 in each phase.

We may extend this definition of the relative surface excess to the total mass per unit area in the surface :

$$\Gamma_{T1} = \Gamma_{T}^{a} - \Gamma_{1}^{a} \frac{\rho^{'} - \rho^{''}}{\rho_{1}^{'} - \rho_{1}^{''}} \qquad (3)$$

where Γ_{T1} is the relative excess of total mass in the surface, while Γ_{T}^{a} is the absolute excess of total mass in the surface, Γ_{1}^{a} is the absolute excess of mass of the solvant in the surface, the mean mass densities in the bulk phases are ρ' and ρ'' and the mean mass concentrations of the solvant in both phases are $\rho_{1}^{'}$ and $\rho_{1}^{''}$.

For a pure system (one single component) the relative excess of mass is identical to the absolute excess of mass and is equal to zero. The situation is quite different if surface active materials are present in the system. If the surface excess of the solvant is chosen equal to zero, the sum of the surface excesses of the surfactants gives the value of the surface excess of total mass.

In a very simple way, Goodrich already showed that with the Gibbs convention it is possible to give a quantitative definition of the surface viscosity coefficients as capillary excess viscosities. As this problem has now taken a renewal of interest through the methods of asymptotic analysis and through the introduction of the second gradients in the developments of the local properties of the interfacial layer, (see for instance [3])we will recall here the very elegant and simple method developed by our late friend and colleague F.C.Goodrich.

1. The momentum balances in a capillary layer.

The capillary layer is characterized by a region of finite size in which the density varies continuously but very sharply from one bulk phase to the other bulk phase. Under static conditions, in the interior of the bulk phases adjacent to the layer, the static pressure tensor $\hat{P}$ is isotropic while in the interfacial region it becomes an axially symmetric tensor with two independant components p_T and p_N. If the fluids are in motion, viscous terms must be added to the static pressure tensor. In the two bulk phases the pressure tensor is

$$\hat{P} = \begin{pmatrix} p + \pi_{xx} & \pi_{xy} & \pi_{xz} \\ \pi_{yx} & p + \pi_{yy} & \pi_{yz} \\ \pi_{zx} & \pi_{zy} & p + \pi_{zz} \end{pmatrix} \qquad (4)$$

while in the interfacial region it is

$$\hat{P} = \begin{pmatrix} p_T + \pi_{xx} & \pi_{xy} & \pi_{xz} \\ \pi_{yx} & p_T + \pi_{yy} & \pi_{yz} \\ \pi_{zx} & \pi_{zy} & p_N + \pi_{zz} \end{pmatrix} \qquad (5)$$

If the fluids as well as the layer are supposed to be Newtonian, the following phenomenological equations hold in the bulk phases

$$\begin{aligned} P_{xx} &= p - (\lambda + 2\eta)\frac{\partial v_x}{\partial x} - \lambda \frac{\partial v_y}{\partial y} - \lambda \frac{\partial v_z}{\partial z} \\ P_{yy} &= p - (\lambda + 2\eta)\frac{\partial v_y}{\partial y} - \lambda \frac{\partial v_x}{\partial x} - \lambda \frac{\partial v_z}{\partial z} \\ P_{zz} &= p - (\lambda + 2\eta)\frac{\partial v_z}{\partial z} - \lambda \frac{\partial v_x}{\partial x} - \lambda \frac{\partial v_y}{\partial y} \end{aligned} \qquad (6)$$

$$P_{xy} = -2\eta\frac{\partial v_x}{\partial y} \quad ; \quad P_{xz} = -2\eta\frac{\partial v_x}{\partial z} \quad ; \quad P_{yz} = -2\eta\frac{\partial v_y}{\partial z}$$

where λ and η are the Lamé coefficients. In the layer however, the axially symmetric tensor of fourth order has at most five independant components. We then have assumed the following constitutive equations

$$P_{xx} = p_T - (\lambda_T + 2\eta_T)\frac{\partial v_x}{\partial x} - \lambda_T \frac{\partial v_y}{\partial y} - \lambda_N \frac{\partial v_z}{\partial z}$$

$$P_{yy} = p_T - (\lambda_T + 2\eta_T)\frac{\partial v_y}{\partial y} - \lambda_T \frac{\partial v_x}{\partial x} - \lambda_N \frac{\partial v_z}{\partial z} \qquad (7)$$

$$P_{zz} = p_N - (\lambda_N + 2\eta_N)\frac{\partial v_z}{\partial z} - \lambda_T \frac{\partial v_x}{\partial x} - \lambda_T \frac{\partial v_y}{\partial y}$$

$$P_{xy} = -\eta_T\left(\frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x}\right) \quad ; \quad P_{xz} = -\eta_N\left(\frac{\partial v_x}{\partial z} + \frac{\partial v_z}{\partial x}\right) \quad ; \quad P_{yz} = -\eta_N\left(\frac{\partial v_y}{\partial z} + \frac{\partial v_z}{\partial y}\right)$$

in which only four different Lamé coefficients appear : λ_T , λ_N , η_T , η_N

An alternative formulation was given by Goodrich. Indeed, he proposed five different Lamé coefficients : λ_T , λ_N , η_T , η_N , η_{Tz} and he wrote the constitutive equations

$$P_{xx} = p_T - (\lambda_T + 2\eta_T)\frac{\partial v_x}{\partial x} - \lambda_T \frac{\partial v_y}{\partial y} - \lambda_N \frac{\partial v_z}{\partial z}$$

$$P_{yy} = p_T - (\lambda_T + 2\eta_T)\frac{\partial v_y}{\partial y} - \lambda_T \frac{\partial v_x}{\partial x} - \lambda_N \frac{\partial v_z}{\partial z} \qquad (8)$$

$$P_{zz} = p_N - (\lambda_N + 2\eta_N)\frac{\partial v_z}{\partial z} - \lambda_N \frac{\partial v_x}{\partial x} - \lambda_N \frac{\partial v_y}{\partial y}$$

$$P_{xy} = -\eta_T\left(\frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x}\right) \quad ; \quad P_{xz} = -\eta_{Tz}\left(\frac{\partial v_x}{\partial z} + \frac{\partial v_z}{\partial x}\right) \quad ; \quad P_{yz} = -\eta_{Tz}\left(\frac{\partial v_y}{\partial z} + \frac{\partial v_z}{\partial y}\right)$$

These equations are then combined with the momentum balance in the absence of external force

$$\rho\frac{d\vec{v}}{dt} = -\,\mathrm{Div}\,\hat{P} \qquad (9)$$

2. Integration through the layer of the momentum balances.

In the capillary layer the pressure tensor is given by eq.(7) or (8) according to the description chosen. In the adjacent bulk phases it is given by eq.(6). To extend the method of Gibbs to dynamic situation one has to introduce the excess surface quantities. It means that we have to integrate across the interface the difference of the divergence of the pressure tensor in the layer and the divergence of the tensor of the two bulk phases extrapolated to the arbitrary division surface chosen. For a plane interface, integration of eq.(9) across the interface gives

$$\frac{d}{dt}\int_I^{II} \rho v_x \, dz = \Delta_s p_{xz} + \int_I^{II} \left[\frac{\partial p_{xx}}{\partial x} + \frac{\partial p_{xy}}{\partial y}\right] dz \qquad (10)$$

$$\frac{d}{dt}\int_I^{II} \rho v_y \, dz = \Delta_s p_{yz} + \int_I^{II} \left[\frac{\partial p_{xy}}{\partial x} + \frac{\partial p_{yy}}{\partial y}\right] dz \qquad (11)$$

$$\frac{d}{dt}\int_I^{II} \rho v_z \, dz = \Delta_s p_{zz} + \int_I^{II} \left[\frac{\partial p_{xz}}{\partial x} + \frac{\partial p_{yz}}{\partial y}\right] dz \qquad (12)$$

Introducing now the constitutive equations (7) or (8) into the integrated balances (10) - (12) and introducing the two-dimensional divergence of v : $\theta = \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y}$ we obtain either

tangential balances

$$\frac{d}{dt}\int_I^{II} \rho v_x \, dz = \Delta_s p_{xz} - \frac{\partial}{\partial x}\int_I^{II} p_T dz + \frac{\partial}{\partial x}\int_I^{II} \left[\lambda_T - \lambda_N + \eta_T\right] \theta \, dz + \nabla_s^2 \int_I^{II} \eta_T v_x dz \qquad (13)$$

$$\frac{d}{dt}\int_I^{II} \rho v_y \, dz = \Delta_s p_{yz} - \frac{\partial}{\partial y}\int_I^{II} p_T dz + \frac{\partial}{\partial y}\int_I^{II} \left[\lambda_T - \lambda_N + \eta_T\right] \theta \, dz + \nabla_s^2 \int_I^{II} \eta_T v_y dz \qquad (14)$$

normal balance

$$\frac{d}{dt}\int_I^{II} \rho v_z \, dz = \Delta_s p_{xz} + \int_I^{II} \eta_N \frac{\partial \theta}{\partial z} dz + \nabla_s^2 \int_I^{II} \eta_N v_z dz \qquad (15)$$

or according to the Goodrich's choice

angential balances

$$\frac{d}{dt}\int_I^{II} \rho v_x \, dz = \Delta_s p_{xz} - \frac{\partial}{\partial x}\int_I^{II} p_T dz + \frac{\partial}{\partial x}\int_I^{II} \left[\lambda_T - \lambda_N + \eta_T\right] \theta \, dz + \nabla_s^2 \int_I^{II} \eta_T v_x dz \qquad (13bis)$$

$$\frac{d}{dt}\int_I^{II} \rho v_y \, dz = \Delta_s p_{yz} - \frac{\partial}{\partial y}\int_I^{II} p_T dz + \frac{\partial}{\partial y}\int_I^{II} \left[\lambda_T - \lambda_N + \eta_T\right] \theta \, dz + \nabla_s^2 \int_I^{II} \eta_T v_y dz \qquad (14bis)$$

normal balance

$$\frac{d}{dt}\int_I^{II} \rho v_z \, dz = \Delta_s p_{xz} + \int_I^{II} \eta_{Tz}\frac{\partial \theta}{\partial z} dz + \nabla_s^2 \int_I^{II} \eta_{Tz} v_z dz \qquad (15bis)$$

where Δs is the difference across the interface, $\theta = \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y}$ and ∇_s^2 is the two-dimensional Laplace operator.

3. The discontinuous model of surface.

We now have to substract from these balances the balances obtained for the discontinuous model system. In this abrupt model of interface we write, introducing the Heaviside step function h(z),

$$\begin{aligned}
&\lambda_T = \lambda_N = \lambda \\
&\rho = \frac{1}{2}\left(\rho^I + \rho^{II}\right) + \frac{1}{2} h(z)\left(\rho^{II} - \rho^I\right) \\
&p_T = p_N = \frac{1}{2}\left(p^I + p^{II}\right) + \frac{1}{2} h(z)\left(p^{II} - \rho^I\right) \\
&\eta_T = \eta_N = \eta_{Tz} = \frac{1}{2}\left(\eta^I + \eta^{II}\right) + \frac{1}{2} h(z)\left(\eta^{II} - \eta^I\right)
\end{aligned} \qquad (16)$$

In this discontinuous model, the velocities are continuous at the surface but the derivatives $\frac{\partial v_x}{\partial z}$ and $\frac{\partial v_y}{\partial z}$ are discontinuous as well as $\frac{\partial^2 v_z}{\partial z^2}$.

We may now define like in the Gibbs treatment the following surface excess quantities :

a) $$\Gamma = \int_I^{II} \left(\rho - \frac{1}{2}\left(\rho^I + \rho^{II}\right) - \frac{1}{2} h(z)\left(\rho^{II} - \rho^I\right)\right) dz \qquad (17)$$

which is the surface excess of mass. This quantity is zero if the system includes one single component and if the dividing surface is chosen in such a way that the integral in (17) vanishes. For a multicomponent system, the situation can be totaly different, especially if surface active substances are present. In that case, one often chose a dividing surface that corresponds to a zero surface excess of the solvant the total mass excess is then the sum of the excesses of the solutes,

b) $$\varepsilon = \int_I^{II} \left(\eta_T - \frac{1}{2}\left(\eta^I + \eta^{II}\right) - \frac{1}{2} h(z)\left(\eta^{II} - \eta^I\right)\right) dz \qquad (18)$$

where ε is the surface excess shear viscosity and

c) $$\kappa = \int_I^{II} \left(\lambda_T - \lambda_N + \eta_T - \frac{1}{2}\left(\eta^I + \eta^{II}\right) - \frac{1}{2} h(z)\left(\eta^{II} - \eta^I\right)\right) dz \qquad (19)$$

where κ is the surface excess dilational viscosity.

We now may also recall the Bakker's equation [4] defining the surface tension σ

$$\sigma = \int_I^{II} \left(p_N - p_T\right) dz \qquad (20)$$

The result of the integration across the interface of the difference of the balance equations in the layer and the balances in the discontinuous model is then

$$\frac{d}{dt}\Gamma v_x^s = \Delta_s p_{xz} - \frac{\partial \sigma}{\partial x} + \kappa \frac{\partial \theta^s}{\partial x} + \varepsilon \nabla_s^2 v_x^s \qquad (21)$$

$$\frac{d}{dt}\Gamma v_y^s = \Delta_s p_{yz} - \frac{\partial \sigma}{\partial y} + \kappa \frac{\partial \theta^s}{\partial y} + \varepsilon \nabla_s^2 v_y^s \qquad (22)$$

These equations correspond to the equations commonly used by the surface hydrodynamicists like Brenner and Wasan [5](the inertial term is however often neglected), but the treatment has the interest to make the bridge between the surface viscosities introduced heuristically and excess properties defined in a more correct way.

For the normal balance, the problem is quite a bit different because, for a planar interface, one only finds the classical result that the difference of pressure across the surface is zero. However, for curved systems one has to handle more carrefully the normal momentum balance. Indeed it now will give rise to a generalization of the Laplace law in dynamical systems. For instance, for a sphere of radius R , one obtains

$$\frac{d}{dt}\Gamma v_r^s = \Delta_s P_{rr} - \frac{2\sigma}{R} - \varepsilon' \left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial v_r}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial v_r}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 v_r}{\partial \phi^2}\right]_{r=R} \qquad (23)$$

where $$\varepsilon' = \int_I^{II} \left(\eta_{\theta r} - \eta_r\right) dr \qquad (24)$$

if we adopt the five different viscosity coefficients like in Goodrich decomposition. But, if we adopt the phenomenological equations (7) with η_r for the shear coefficient in the normal planes, the last term of eq.(23) vanishes. However, R.Aris [6]has introduced a surface viscosity term in his normal surface balance equation : he wrote for a surface without inertial term

$$\Delta_s P_\pi = \frac{2\sigma}{R} + \frac{2\kappa}{R}\left[\frac{1}{R\sin\theta}\left[\frac{\partial}{\partial\theta}\left(v_\theta \sin\theta\right) + \frac{\partial v_\phi}{\partial\phi}\right]\right] \qquad (25)$$

where he calls κ the dilational surface viscosity coefficient. It seems thus that there exists a contradiction between our results and the equations heuristically introduced by Aris.

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EXTENDED IRREVERSIBLE THERMODYNAMICS : TOWARDS A NON-LOCAL FORMULATION

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Abstract : In the first part of this note, we briefly recall the motivations and the basic hypotheses underlying extended irreversible thermodynamics. To illustrate the application of the formalism, one considers the problem of a viscous fluid subject to thermal heating : the relevant constitutive equations are established and their relation with the classical formulation is discussed. Extended Thermodynamics appears to be useful in treating materials involving large relaxation times (like dielectrics at low temperature, polymers, ...) and high-frequency and short-wavelength processes (ultrasounds, light and neutron scattering, ...). However to deal with short-wave length phenomena, it is imperious to introduce non-locality in space. This is achieved by including supplementary variables taking the form of fluxes of the fluxes. The corresponding changes in the expression of the constitutive equations and the entropy flux are discussed.

Extended Irreversible Thermodynamics (EIT) is born out of the necessity to enlarge the range of applicability of classical irreversible thermodynamics to large frequencies and short wave-lengths phenomena. EIT is particularly well suited for describing ultrasonic wave-propagation, heat propagation in dielectrics at low temperature (phonon hydrodynamics), shock waves, light and neutron scattering in liquids and gases as well as materials involving long relaxation times like polymeric solutions, dielectric materials, superfluids and superconductors.

The basic idea in EIT is to extend the space of state variables by including the flux of matter, flux of momentum and flux of energy among the set of basic variables.

Denoting by V the space of variables, it will be formed by the union $C \cup J$ of the set of classical variables C (like mass, velocity and energy) and the flux variables J. The classical variables C obey the well-known conservation laws of mass, momentum and energy while the extra variables J are supposed to satisfy Markovian evolution equations of the form

$$\dot{\boldsymbol{J}} = -\nabla.\boldsymbol{F}^{J} + \sigma^{J} \tag{1}$$

a dot stands for the time derivative (either the material or any "objective" time derivative), $\boldsymbol{J}^{F}$ is the flux of flux $\boldsymbol{J}$ and σ^{J} a source term. The closure of the set of evolution equations is ensured by expressing $\boldsymbol{F}^{J}$ and σ^{J} in terms of the whole set V of variables

by means of constitutive equations. Since the final results have to comply with the second law of thermodynamics, one must introduce a non-equilibrium entropy. The latter is supposed to be a convex potential function of the whole set V of variables and its rate of production is supposed to be non-negative.

To illustrate these general ideas, consider the motion of an incompressible mono-component fluid subject to heating. The basic variables are velocity, energy (or temperature T) plus the corresponding fluxes, namely the viscous stress tensor σ and the heat flux vector $\boldsymbol{q}$. The relevant evolution equations are the classical momentum and energy balance laws plus the evolution equations for the heat flux and the viscous stress tensor (for simplicity the latter is assumed to be symmetric and traceless) :

$$\dot{\boldsymbol{q}} = -\nabla.\boldsymbol{F}^q + \sigma^q \tag{2}$$

$$\dot{\sigma} = -\nabla.\boldsymbol{F}^v + \sigma^v \tag{3}$$

where the unknown quantities $\boldsymbol{F}^q, \sigma^q, \boldsymbol{F}^v$ and σ^v will be given by constitutive equations.

From the positiveness of the entropy production σ^s defined through

$$\sigma^s = \rho\dot{s} + \nabla.\boldsymbol{J}^s \geq 0 \tag{4}$$

wherein the entropy density s and the entropy flux $\boldsymbol{J}^s$ are expressed by means of constitutive relations $s = s(V)$ and $\boldsymbol{J}^s = \boldsymbol{J}^s(V)$, it is shown that equations (2) and (3) take the form

$$\tau_1\dot{\boldsymbol{q}} = -(\boldsymbol{q} + \lambda\nabla T) + \beta\nabla.\sigma \tag{5}$$

$$\tau_2\dot{\sigma} = -\left(\sigma - \eta(\nabla \boldsymbol{v})^{sym}\right) + \beta\,\nabla\boldsymbol{q} \tag{6}$$

By formulating (5) and (6), one has omitted quadratic and higher order terms in the fluxes. The undefined quantities in (5) and (6) are : λ the heat conductivity, η the dynamic shear viscosity, $\boldsymbol{v}$ the velocity, τ_1 and τ_2 the relaxation times, β a coupling parameter, the same β appears in both relations (5) and (6) because of Onsager's reciprocity property. It is also shown that $\boldsymbol{J}^s$ will be given by

$$\boldsymbol{J}^s = \frac{\boldsymbol{q}}{T} + \beta\,\sigma.\boldsymbol{q} \tag{7}$$

while s obeys a generalized Gibbs equation

$$ds = T^{-1}du - \frac{\tau_1}{\lambda T^2}\boldsymbol{q}.d\boldsymbol{q} - \frac{\tau_2}{\eta T}\sigma:d\sigma \tag{8}$$

From $\sigma^s > 0$, it is inferred that

$$\lambda > 0 \quad \eta > 0 \tag{9}$$

while the convexity property of s implies that

$$\tau_1 > 0 \quad \tau_2 > 0 \tag{10}$$

Expressions (5) and (6) contain as particular cases the classical Fourier law for heat conduction and Newton's law of hydrodynamics by letting τ_1, τ_2 and β vanish. By setting in (5) and (6), the coupling parameter β equal to zero, one recovers the Cattaneo-Vernotte and Maxwell relations, namely

$$\tau_1 \dot{\boldsymbol{q}} = -\boldsymbol{q} - \lambda \nabla T \tag{11}$$

$$\tau_2 \dot{\sigma} = -\sigma + \eta (\nabla \boldsymbol{v})^{sym} \tag{12}$$

However, even the rather general relations (5) and (6) reveal too crude to describe high frequency and high wave-number phenomena as ultrasound propagations and light and neutron scattering by fluids. Moreover, it is expected that systems with very short characteristic wavelengths, like micro-devices and interfaces, require a non-local description. Within the framework of EIT, this can be achieved in a rather systematic way by introducing additional variables; these extra variables may take the form of fluxes of fluxes. For instance in the problem of heat conduction, Cattaneo-Vernotte equation, written as

$$\tau^{(1)} \dot{\boldsymbol{q}}^{(1)} = -\nabla . \boldsymbol{q}^{(2)} - \lambda \nabla T \tag{13}$$

should be complemented by evolution equations for the fluxes of flux $\boldsymbol{q}^{(2)}, \boldsymbol{q}^{(3)} \ldots \boldsymbol{q}^{(n)}$:

$$\tau^{(2)} \dot{\boldsymbol{q}}^{(2)} = -\nabla . \boldsymbol{q}^{(3)} - \sigma^{(2)} \tag{14}$$

$$\tau^{(n)} \dot{\boldsymbol{q}}^{(n)} = -\nabla . \boldsymbol{q}^{(n+1)} - \sigma^{(n)} \tag{15}$$

For simplicity, consider only $\boldsymbol{q}^{(1)}$ and $\boldsymbol{q}^{(2)}$ as variables and express $\sigma^{(2)}$ and $\boldsymbol{q}^{(3)}$ by means of constitutive equations. At the lowest order of approximation, one has

$$\sigma^{(2)} = a \boldsymbol{q}^{(2)}, \qquad \boldsymbol{q}^{(3)} = b \boldsymbol{q}^{(1)} \boldsymbol{I} \tag{16}$$

wherein a and b are arbitrary scalar functions of the temperature and $\boldsymbol{I}$ stands for the identity tensor. Assuming that $\tau^{(2)} << \tau^{(1)}$, one may eliminate $\boldsymbol{q}^{(2)}$ between (13) and (14) so that the final result will be

$$\tau^{(1)} \dot{\boldsymbol{q}} = -\boldsymbol{q} - \lambda \nabla T - \gamma \nabla^2 \boldsymbol{q} \tag{17}$$

wherein we have dropped super index (1). Expression (17) contains a non-local term in $\nabla^2 \boldsymbol{q}$ and is referred to in the literature as Ginzburg-Landau or Guyer-Krumshal type equation.

It should be mentioned that non-locality can be introduced into EIT without using higher order fluxes, whose physical meaning is not always easy to assign, at least at the macroscopic level of description. One may for instance express the fluxes $\boldsymbol{F}^q$ and $\boldsymbol{F}^v$ defined through equations (2) and (3) in terms of the gradient of the whole set of variables. To be explicit, if $\boldsymbol{F}^q$ contain a term in $\nabla \boldsymbol{q}$ and $\boldsymbol{F}^v$ a term in $\nabla \sigma$, then the evolution equations (5) and (6) for $\boldsymbol{q}$ and σ will be generalized as

$$\tau_1 \dot{\boldsymbol{q}} + \boldsymbol{q} + \lambda \nabla T = -\lambda T^2 \beta \nabla . \sigma - L_2 \nabla . \nabla \boldsymbol{q} \tag{18}$$

$$\tau_2 \dot{\sigma} + \sigma - \eta (\nabla \boldsymbol{v})^{sym} = -\eta T \beta \, \nabla \boldsymbol{q} - l_2 \nabla^2 \sigma \tag{19}$$

which contain "second gradients" of $\boldsymbol{q}$ and σ.

It is worth emphasizing that the above results (18) and (19) refer to weak non-locality as non-local effects are truncated at second order terms in the gradients. It is nevertheless hoped that such a approximation will be sufficient for describing a wide majority of non-local effects.

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" COMPUTER MODELLING OF FUNDAMENTAL EQUATIONS FOR SURFACES"

Report summary to Network group meeting

held at C N R S Bellevue, Meudon 13th - 16th Oct 1994

By J F Padday

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INTRODUCTION

Over the past 100 years, the development of fundamental equations representing the behaviour or state of a liquid-fluid interface has followed Gibbsian thermodynamic laws. By applying these equations to systems at constant temperature, a mechanical description of the local equilibrium, is given in terms of simple general equations such as the Young-Laplace equation for capillary pressure and Young's contact angle equation. Though useful in applications to experiment, the inherent problems of applying the equations to describe a system at equilibrium is that only the local equilibria are examined whilst that of the whole system remain generally unclear and in multiple fields, not understood at all.

The purpose of this study is to set out the types of thermodynamic equilibria of a system (with an axis or a plane of symmetry) involving one or more liquid interface; then to determine the values of the variables at these equilibria ; and finally, to show by computer simulation that the system may be mechanically perturbed to provide non-equilibrium data from which the degree of stability may be evaluated and the pathway of mechanical breakdown of the drop during its preliminary stages of breakaway.

TYPES OF EQUILIBRIA

The Gibbs thermodynamic equilibrium is inconsistent with the Laplace capillary equation which is derived on purely mechanical grounds, and thus any extension of a surface during a perturbation must be regarded as being both isothermal and adiabatic. Even so, here Laplace's reasoning will be followed on the basis that the mechanical treatment is sufficiently precise for experimental purposes.

The equilibrium relating surface curvature to the pressure across the interface, is a local equilibrium and applies only at positions where the potential of the applied field is uniform. In a gravity field this is a horizontal plane, in a rotational field a cylinder and in an electrical field a ring.

Three types of equilibria are distinguished:

Stable equilibrium	where	$d^2E/d\phi^2 > 0$
Unstable equilibrium		$d^2E/d\phi^2 < 0$
Critical equilibrium		$d^2E/d\phi^2 = 0$

where E is the total free energy of the system and ¢ is the perturbation which is of mechanical nature and involves a change in surface area. Finally it is noted that th stability criteria are entirely different for systems that are perturbed at constar volume of liquid as compared to those perturbed at constant capillary pressure. A futhe subdivision of perturbation depends on whether the solid surface supporting the liqui is at constant radius or constant contact angle.

EQUATIONS OF STATE IN A FORCE FIELD

The following types of force field form a part of this study:

No force field	---	Microgravity
Natural Terrestrial gravity	---	Normal laboratory conditions
Rotational Inertia field	---	Rotating drops with or without gravity
Electric field	---	Conducting liquids
Magnetic field	---	Ferrofluids

The following equations express the local equilibria in a force field:

Young- Laplace's capillary equation

$$P = \gamma (1/ R_h + 1/R_v)$$

which may be expressed in differential form (Gauss - Poisson) as

$$\frac{\partial^2 z/\partial^2 x}{(1+(\partial z/\partial x)^2)^{3/2}} + \frac{\partial z/\partial x}{x(1+(\partial z/\partial x)^2)^{1/2}} = C$$

With gravity acting along Z axis

$$X_n/R_h + X_n/R_v = C_n \ (1+ Z /X_n)$$

where $(k/X_n)^2 = \sigma/ \rho\ g = 1/C_n$

With rotation on axis of symmetry

$$X_n/R_h + X_n/R_v = C_n + W_r.(d/k)^2 \ . \ fX^2 \ dv/d^5$$

where $W_r = \pi.\Omega^2 \Delta\rho\ d^3/\sigma$

With electrostatic charge

$$X_n/R_h + X_n/R_v = C_n + N_c. H^2.\{R/k\}^2 \ fE.dV$$

where $N_c = R.U^2 /(2.\sigma h^2)$

With magnetic field

of the form but no finally corrected

$$X_n/R_h + X_n/R_v = C_n + Bo_m H^2 f \ \pi.X^2.dZ$$

where $Bo_m = \phi M_s h /M \sigma$

Each of the above equations may be used to form a composite equation in differential form to express the local equilibrium of an axially symmetric interfacial system in one or more of the force fields given above.

It has been found that the standard state of the system in each force field must first be established so that any change of shape induced by one field effectively changes the contribution of the other. For instance, in a gravity field the standard of the liquid will be located at some point either inside or outside the system where the capillary pressure is zero and the equilibrium surface would be flat.

Having now established the local equilibrium the next step is to integrate the local energy equation so as to calculate the energy of the whole system.

THE NUMERICAL INTEGRATION PROCEDURE

The modelling process is applied to a pendant or sessile drop and in a field where the strength and other properties of the system are defined. The starting point is taken at the position where the profile of the drop crosses the axis of symmetry at which point the two radii of curvature are equal and the properties of a spherical cap apply.

Integration then proceed using fourth order RUNGE KUTTA with the distance along the profile taken as the independant variable, As the integration proceeds along the profile other properties of the drop are interpolated on the way. The following list of properties are derived at each point on the profile:

Angle subtended at the axis of symmetry; Radial distance X; Distance from origin Z;

Distance along profile F; Horizontal Radius of curvature R_h; Vertical Radius R_v ;

Total area A; Total Volume V; Total Energy E_t ;

Interpolation of the properties may be demanded at given values of any of the above properties or their derivatives.

The most useful form of the data was to generate shape tables covering a range of appropriate Bond numbers and then exploring properties in graphical form.

GENERATING NON-EQUILIBRIUM DATA ENERGY PROFILES

The above procedures generate only equilibrium data. However it has been found that if the system is perturbed artificially (ie mathematically), non-equilibrium data may be extracted too, using the same Runge Kutta procedures.

The energy properties of a drop at a fixed ratio of V/X^3 where the volume of the drop is V, and the tip radius is X, are extracted from each of a number profile shapes of differing Bond number. These properties are now scaled to a constant value of X/k . The effect of this is to produce an array of data which forms the energy profile of the drop. Two of this set of values will be at equilibrium and all others will be at non-equilibrium. These non-equilibrium states may be regarded as the transient shape the drop would adopt if placed in a weaker or stronger field but with the total energy being that of the perturbed shape in the given field.

The energy profile is of cubic form and with a definite trough and a maximum on a hump. The energy minimum in the trough is the stable equilibrium and the maximum is the unstable equilibrium. For a given tip radius the difference between the stable and unstable properties diminisnes as the drop volume increases until at maximum volume the two points merge and the pendant drop becomes critically stable at which point it drops away.

BREAKAWAY OF THE DROP

The energy profile of the critical drop further predict the cascade of shapes through which the breakaway drop passes as it begins its descent in the gravity field. The drop then passes into an evolutionary stage where viscosity determines the path by which the drop finally breaks away.

CONCLUSIONS AND FURTHER WORK

So far the computer simulation suggests that a wide variety of critical instabilities may be followed using this simulation techniques. The computer programme is run on a Hewlett Packard 9000/300 workstation programmed in HP.Basic. However, an attempt is being made to transfer the whole programme (2500 statements) to a Apple Macintosh written in c++. For this purpose further hardware and software are required as well as a crash course in C++ programming.

The equations for the shape of a drop in the force fields described above are very satisfactory providing that the magnetic field effect is excluded. The derivation of the effects of a magnetic field on a drop require further fundamental analysis prior to modelling on a computer.