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WORKSHOP ON SPACE PHYSICS:
"Materials in Micorgravity"
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"Fundamentals of Microgravity Fluidynamics"

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INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
TRIESTE - ITALY

WORKSHOP ON SPACE PHYSICS:
MATERIALS in MICROGRAVITY

LECTURE NOTES ON:

FUNDAMENTALS of MICROGRAVITATIONAL FLUIDYNAMICS

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1. INTRODUCTION

For any system consisting of two phases immiscible there is an interface layer of small thickness whose properties may markedly differ from those of the adjacent bulk phases and wherein the action of short range forces between the molecules of the two phases is predominant.
The study of interface layers from the molecular point of view is dealt with by other lectures. Here we consider the macroscopic point of view.

Up to few years ago the treatment of the thermodynamics and dynamics of interface layers hinged on rather strong simplifying hypothesis which were justified, to a certain extend, by the very nature of problems addressed.
In thermodynamics studies, the bulk phases assumed to be homogeneous, uniform, quiescent, steady, and in equilibrium with the layer.
A key role was played by the concept of "dividing surface" introduced by Gibbs. The interface layer is replaced by a surface (referred to as Gibbs' surface) and the bulk phases are assumed to extend, with their uniform properties, up to it.
The equivalence between the model and the layer is restored by assigning to the dividing surface the masses resulting from the

difference between the model and actual layer (referred to as "excess" masses). The excess quantities depend on the location of Gibbs' surface within the layer. The surface is given a free energy which depend on its area and on "excess" masses.

For a simple component system (a liquid and its vapor) the location of Gibbs' surface in chosen as to make the excess mass zero. Hence its free energy depends only on the area, the free energy per unit area being interpreted as a surface tension.

For multicomponent systems the degree of freedom in the location of the surface can be used to reduce to zero the excess mass of only one component. Those of the other components, divided by the area of the surface, are usually referred to as adsorption coefficients.

The further assumption of first order homogenity of the surface free energy, coupled with the hypothesis of thermodynamic equilibrium between layer and buljk phases, leads to a relation known as Gibbs' adsorption equation.

This equation has been later generalized to apply to charged and/or polarized layers.

Studies of the dynamics of interfaces had been mainly concerned with so-called capillary phenomena associated with the surface tension. They become significant when either the curvature of the interfacial surface is very large or the surface tension is not uniform over the surface.

A partial list of problems in which surface tension plays an important role is: surface waves; decay of cylindrical jets; capillary waves on the surface of a drop; Marangoni flow (i.e. motions induced by tangential gradients of surface tension); motion in thin liquid films; bubbles and drops dynamics; hydrodynamic stability of moving interfaces; instabilities due to the Marangoni effects.

In these hydrodynamic studies the interface layer is again replaced by a surface but, in general, insufficient attention is given to its thermodynamic properties. The effect of surface-tension on the dynamical evolution of the bulk-phases is modeled through a balance of forces acting on the surface. This balance, in turn, is taken as the boundary conditions to be satisfied by the field equations for the two bulk phases.

Electromechanical studies of coupling at interfaces and of the effect of interface electric stresses were carried out with the same approach. The coupling between surface and bulk-phase phenomena is modeled through the jump form of the hydrodynamic and Maxwell's equation (taken as boundary conditions for the volume field equations) and the interface is considered devoid of any thermodynamic property beside the surface tension.

These rather naive modelling of thermodynamics and dynamics of interfaces resulted often justified by the nature of the problems considered.

The inadequacy of the modelling was at times acknowledged but there was no real stimulus of its further refinement also because its potentialities have not been fully explored and much numerical work and experimental investigations still have to be carried out for the complete mastery of the problems for which this simple modelling is adequate.

The prospect of materials processing in space and of space manufacturing have changed the prevailing scenario for a number of reasons. On one hand, in a low or micro-gravitational environment surface tension driven phenomena acquire a much more relevant role in many more situations than in the normal gravitational environment. Thus, for instance, it has clearly appeared that mastering surface driven convection phenomena is microgravitational environment is an absolute prerequisite for designing meaningful crystal-growth experiments in space and; later on, for the successful achievement of materials processing in space.

Hence the need soon arose for a better and more realistic modelling of both the thermodynamics and the dynamics od interfaces.

Thus, for instance, numerical investigations of thermally induced Marangoni flows in a floating zone (a problem intimately connected with one of the possible schemes for crystal-growth) require "thermal" boundary conditions on the free surface of the zone. The proper formulation of these boundary conditions cannot be achieved, as customary with the previously mentioned "hydrodynamic" approach, by simply writing a jump form of the internal energy balance equations. By thus doing, equilibrium and non equilibrium thermodynamic properties of the surface are unduly ignored and the results have no physical relevance. What is needed is a surface balance equation which, in turn, presupposes an adequate modelling of the thermodynamics of the surface itself.

On the other hand, the availability of space laboratories has provided a strong stimulus for deeper studies of complex interface phenomena for their own scientific interest in addition to their relevance in application to material sciences.

This being the present scenario, it is clear that a coherent, unitarian and rigorous macroscopic modelling of the thermodynamics and dynamics of interfaces is both an absolute prerequisite for meaningful numerical simulations and a useful support to experimental investigations.

Aim of these lectures is to present the latest results in the macroscopic modeling of the thermodynamics and dynamics of interfaces which accounts for the following general aspects not all considered in the simpler models:

i) The bulk phase and the interface layer may not be uniform and quiescent;

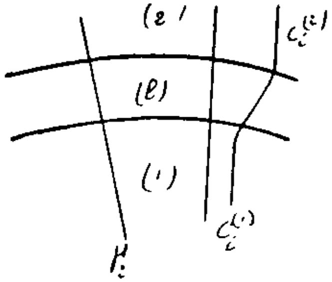
ii) The interface layer may not be in equilibrium with the adjacent bulk-phases;

iii) The field may be unsteady.

Non-uniformity and non equilibrium refer to any couple of energy conjugate extensive and intensive properties.

It will be briefly discussed here in terms of the mass Mi of a constituent and of the chemical potential μ_i , its intensive parameter conjugated with respects to the energy.

Conditions of uniformity and mutual equilibruim between interface layer and bulk phases are schematically shown in the figure.

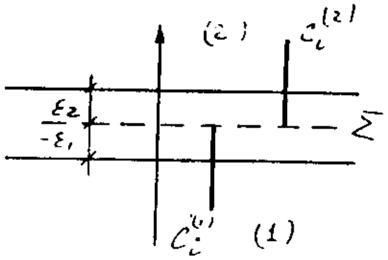


The chemical potential μ_i is constant both in the bulk phases and across the layer. Thus, if superscripts 1, 2, ℓ denote, respectively, values for the two bulk phases and the layer, it is:

$$\mu_i^{(1)} = \mu_i^{(2)} = \mu_i^{(\ell)}$$

and this common value is the same throughout. The concentration $c_i = M_i / M$ (where M is the total mass) has a profile which is independent of the station along the layer. The concentration is constant in the two bulk phases and varies continuously across the layer from its value in one bulk phase to its value in the other bulk phase.

In the Gibbs model the layer of thickness $\varepsilon = \varepsilon_1 + \varepsilon_2$ (see figure) is replaced by the dividing surface Σ .



The total volume V occupied by the bulk-phase and the layer is subdivided as :
$V = V^{(1)} + V^{(2)}$ and the subvolume $V^{(j)}$ (j= 1, 2) is filled by the j-th uniform bulk phase. The total mass of the i-th component present in the actul system is:

$$m_i = m^{(1)} + m^{(2)} + m^{(\ell)}$$

and, in the model:

$$m_i = \rho_i^{(1)} V^{(1)} + \rho_i^{(2)} V^{(2)} + m^{(s)}$$

where $\rho_i^{(j)}$ is the mass density in the j-th bulk phase and $m^{(s)}$ is the mass associated with the dividing surface. The adsorption coefficient Γ_i is defined by:

$$m_i^{(s)} = m_i - \left[\rho_i^{(1)} V^{(1)} + \rho_i^{(2)} V^{(2)}\right] = \Gamma_i A$$

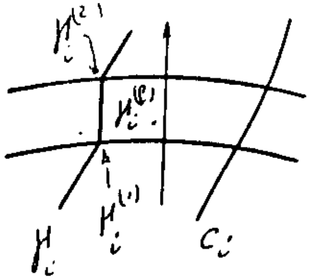
where A is the area of the surface. It clearly depends on the location of Σ within the layer (characterizing the partition $V = V^{(1)} + V^{(2)}$ and can be positive, negative or null).

It is to be pointed out that, even in this case, another alternative is possible. One can indeed associate to the surface Σ not the previously defined excess mass Mi, but rather the actual mass $m_i^{(\ell)}$ present in the layer. One is thus lead to define a surface density $\tilde{\rho}_i$ of the (i-th) component by letting:

$$m_i^{(\ell)} = \tilde{\rho}_i A$$

The surface density thus defined is independent of the actual location of Σ within the layer. This has obvious advantages. However some uncertanty permains since the thickness of the layer (and hence the quantity $Mi^{(\ell)}$ needs to be defined (The same conceptual difficulty is present in the Gibbs' model).

Non uniformities can be present in directions either tangential to the interface or normal to it, and both in the layer and in the bulk phases. Conditions of non uniformity in the volume phases are schematically shown in figure.



The gradient of μ_i normal to the interface is no longer zero, but it is still $\mu_i^{(1)} = \mu_i^{(2)} = \mu_i^{(\ell)}$ where, now, the bulk phase values are evaluated at the edges of the layer (Recall that, in the skecth, the dimensions are much enlarged to adequately represent the layer).

Non uniformities in tangential directions imply that the profiles shown in figure may now change from one station to another.

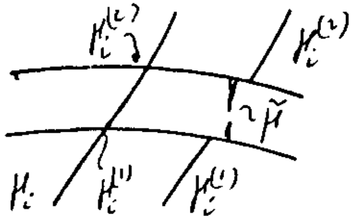
Both types of non-uniformities induce (irreversible) mass diffusion fluxes. The normal gradients at the outer edges of the layer induce exchange of mass of the i-th component between the layer and the bulk phase. Tangential non uniformities within the layer induce mass diffusion within the layer.

For both reasons the layer, as a whole, is no longer in condition of thermodynamic equilibrium and no further modelling is possible if the shifting equilibrium hypothesis is not valid. When such is insteady the case, a local formulation of thermodynamics can be resorted to. In these situations the motion of excess quantities is much less helpful and that of surface densities seems more appropriate.

A further step away from global equilibruim occurs when the chemical potentials at the edges of the interface layer are not equal.

In this case, one can still model the layer as a surface phase but must assign to it a value $\tilde{\mu}_i$ of the chemical potential different from $\mu_i^{(1)}$ and $\mu_i^{(2)}$.

The layer is not in equilibrium with the adjacent volume phases with respect to exchange of mass of the i-th constituent. In the conditions depicted in figure, the layer will receive mass from the volume phase (1) ($\mu_i^{(1)} > \tilde{\mu}_i$) and will give mass to the volume phase (2) ($\tilde{\mu} > \mu_i^{(2)}$). This exchange will be referred to as normal exchange between the layer and the bulk-phases.



Finally, for stronger normal non-uniformities of intensive parameters within the layer one would have to model also diffusion, in the normal direction, <u>within</u> the layer.

What so far said for scalar extensive properties applies to momentum (a vectorial extensive property) when the velocity field is not uniform (recall that the velocity is the intensive parameter conjugated to the momentum with respect to the energy).

To account for the above described phenomenology, the interface layer and the adjacent bulk-phases are modelled as a surface phase in contact with two volume phases.

The surface phase is characterized by its geometry and by its thermodynamic properties. Position and shape of the surface are, in general, function of the time. The shifting equilibrium hypothesis is assumed to hold for both the volume and the surface phases so that a local formulation of thermodynamics applies. It is here supposed that the reader is familiar with the motivations, implications and limits of the macroscopic local formulations as applied to the thermodynamics and dynamics of continous media.

No a priori assumption is made as to the equilibrium with respect to any extensive property.

The study of the surface phase will deal with its equilibrium and non-equilibrium thermodynamics and with its dynamics described by a complete set of surface balance equations. The latter ones reduce to the known jump form of the volume phase balance equations when the surface Σ is devoid of any thermodynamic property.

The outline of the lectures is as follows.

The geometry and simple kinematics of the surface and the local formulation of its equilibrium thermodynamics are first dealt with in general terms.

Subsequently, the surface phase balance equations for arbitrary scalar and vectorial properties are derived and discussed.

The following topics will be considered: equilibrium thermodynamics description and properties of the surface-phase; formulation and discussion of the pertinent set of surface balance equations; derivation of the expression for the surface entropy production density with ensuing identification of generalized forces and fluxes; discussion of the surface phenomenological relations within the framework of linear irreversible thermodynamics; analysis of the complete set of equations and comparison with results of simpler theories.

In the next chapters the non-dimensional balance equations for the bulk and surface phases are presented and an order of magnitude analysis is performed.

2. GEOMETRY AND KINEMATICS OF SURFACE-PHASE

2.1 Introduction

The choise of an appropriate class of coordinate system is a necessary condition for the proper formulation of the volume and surface phases balance equations and of their meaningfull, of the non-dimensional forms, needed, in turn, for a correct non dimensional analysis which should lead, among other things, to information concerning the nature and occurrence of several possible regimes suitably and properly expressed in a-priori forms, that is in terms of problem's geometrical and physical data.
The main requisite determining this choise is the possibility of singling out and evidencing the particular role played-by the direction field represented by the unit normal **n** to the surface S which models the interface. The most general class of coordinate system satisfyng these requirements is the parallel surface coordinate system (p.s.c.s.) in which one family of coordinate system is constituted by the family of surfaces parallel to S and a coordinate is the Euclidean distance (n) from S.
Thus the position vector r(P) of a point P in the Euclidean space E_3, measured from an arbitrary but fixed origin 0, is given, on considering for simplicity the case in which S is fixed in E_3 (a limitation that will be later removed) by

$$\underline{r}(\eta^i) = \underline{r}_0(\eta^\alpha) + n\,\underline{n}(\eta^\alpha) \qquad (2.1)$$

where η^α (here and throughout the latin suffices and/or indices will run from one to three, whereas greeck ones will run from one to two) are arbitrary coordinates on the surface S, $n = \eta^3$ is the Euclidean distance of $P(\eta^i)$ from S and $r_0(P_S)$ is the position vector of the point $P_S(\eta^\alpha) = P(\eta^\alpha, 0)$, projection of $P(\eta^i)$ on S. The coordinate surfaces $n = const = n^*$, parallel to S, are two-dimensional Riemannian varieties $V_2(n)$ with $V_2(0) = S$.

This section will thus be devoted to the study of the geometry of the surface S:

$$\underline{r}(\eta^\alpha, 0) = \underline{r}_0(\eta^\alpha)$$

This study needs to be a thorough one in view also of the fact that, in general, position and form of S may not be known a-priori but will be one of the result of the analysis.
We shall thus have to consider definitions and properties of

- covariant $\{\underline{g}_\alpha\}$, contravariant (dual) $\{\underline{g}^\alpha\}$ basis vectors
- The two fundamental tensors $\underline{\underline{U}}$, (unit tensor on S) and $\underline{\underline{K}}$ (curvature tensor of S), the three fundamental forms of S, Crystoffel symbols
- Covariant and contravariant derivation on S and such related notions as parallel transport.
- Geodesics of S
- First and second order differential operators
- Compatibility (or integrability) conditions leading to the equations of Gauss and Codazzi
- Rieman tensor

Whenever appropriate we shall specialize the general results to the particular case in which the surface coordinates (η^α) are orthogonal and discuss, for instance, the conditions in which they be taken to coincide with the geodesics of S. We shall then discuss the properties of parallel surface coordinate systems. As it easily argued, many of the results found for the Riemanian variety $S = V_2(0)$ are readily extended to the Riemanian varieties $V_2(n)$ parallel to S.

However there are a number of additional questions to be adressed, we shall point them out during the development. The crucial ones we believe is the proof that all operators, algebraic or differential, of interest in the present context, can (and will be) expressed in terms of the first two fundamental tensors of S ($\underline{\underline{U}}_s$ and $\underline{\underline{K}}$) or, equivalently, in terms of the coefficients of its two fundamental forms.

Once this is accomplished, we have at hand all the tools necessary to formulate, in subsequent chapters, the different form (global, local, jump, dimensional and non dimensional) of the balance equations for scalar and vectorial extensive variables for the volume and surface phases.

2.2 Notations

- Cartesian coordinate system.

  Origin:0

  Coordinates y^i (i=1,2,3)

  Unit vectors $\underline{c}_i = \underline{c}^i$

- A vector (tensor) having no components in the direction n normal to S will be denoted with the suffix (s) and, by definition, it is:

$$\underline{F}_s \cdot \underline{n} = 0 \qquad \underline{\underline{T}}_s \cdot \underline{n} = \underline{n} \cdot \underline{\underline{T}}_s = \underline{0}$$

- The two dimensional nabla operator on S will be called surface gradient and denoted by $\underline{\nabla}_s$. Thus:

$$\underline{\nabla}_s = \frac{\partial}{\partial \underline{r}}$$

  and, by definition

$$\underline{n} \cdot \underline{\nabla}_s = 0$$

- The three dimensional unit tensor in E3 will be denoted by and decomposed as

$$\underline{\underline{U}} = \underline{\underline{U}}_s + \underline{n}\,\underline{n}$$

  where $\underline{\underline{U}}_s$ is the two dimensional unit tensor on S

- The unit tensor $\underline{\underline{U}}_s$ acts as a projection operator so that, for an arbitrary vector **F** defined on S its surface projection $\mathbf{F}_S$ is given by

$$\underline{F}_s = \underline{F} \cdot \underline{\underline{U}}_s$$

- Similarly for a second order tensor $\underline{\underline{T}}$ one has

$$\underline{\underline{T}}_s = \underline{U}_s \cdot \underline{\underline{T}} \cdot \underline{\underline{U}}_s$$

- Kronecker symbols:

$$\delta_{ij} \; ; \; \delta_i^j \; , \; \delta_{\alpha\beta} \; ; \; \delta_\alpha^\beta$$

- Einstein summation convention is assumed with latin indices running from 1 to 3, and greek indices running from 1 to 2.

2.3 Geometry of surface S

2.3.1 Representations and covariant basis vectors

The position vector of running point $P_S(\eta^\alpha)$ is

$$\underline{r}_0(P_s) = \underline{c}_i \, y_0^i = \underline{r}_0(\eta^\alpha)$$

where the functions:

$$\eta^\alpha = \eta^\alpha(y_0^i)$$

and their inverse

$$y_0^i = y_0^i(\eta^\alpha)$$

are assumed to be at least of class C_3.

The elementary absolute vector lying in the plane tangent to S in P_S

$$d\underline{r}_0 = \underline{G}_\alpha \, d\eta^\alpha = \underline{c}_i \, dy_0^i$$

define the coordinate basis covariant vectors

$$\underline{G}_\alpha = \frac{\partial \underline{r}_0}{\partial \eta^\alpha} = \frac{\partial y_0^i}{\partial \eta^\alpha} \underline{c}_i$$

The vector $\underline{G}_\alpha$ is in the tangent plane of S in P_S and is tangent to the coordinate line η^β=const.

2.3.2 First fundamental form

The squared length ds_0^2 of the absolute elementary vector gives the first fundamental form $q_1(S)$ of S:

$$q_1(S) = ds_0^2 = d\underline{r}_0 \cdot d\underline{r}_0 = g_{\alpha\beta} \, d\eta^\alpha \, d\eta^\beta \qquad (2.2)$$

where:

$$g_{\alpha\beta} = \underline{g}_\alpha \cdot \underline{g}_\beta = \frac{\partial y_0^i}{\partial \eta^\alpha} \frac{\partial y_0^j}{\partial \eta^\beta} \delta_{ij}$$

are referred to as coefficients of the metrics.

q1(S) is symmetric and positive definite:

$$g_{\alpha\beta} = g_{\beta\alpha}$$

$$g_{\alpha\alpha} > 0 \qquad g_{11} g_{22} - g_{12}^2 = g = \det(g_{\alpha\beta}) > 0$$

when $g_{12} = 0$ the families of curvilinear coordinates are orthogonal.

Properties of S expressed in terms of the coefficients of the first fundamental form (metrics coefficents) are said to be intrinsec: they are invariant with respect of bending of S in E3.

2.3.3 First fundamental tensor.

The bidimensional unit tensor $\underline{\underline{U}}_s$, the surface gradient of the position vector r_0, is the first fundamental tensor of S:

$$\underline{\underline{U}}_s = \underline{\nabla}_s \underline{r}_0 = \frac{\partial \underline{r}_0}{\partial \underline{r}_0} = \underline{g}^\alpha \underline{g}_\alpha$$

where

$$\underline{g}^\alpha = \frac{\partial \eta^\alpha}{\partial \underline{r}_0} = \underline{c}^i \frac{\partial \eta^\alpha}{\partial y_0^i}$$

is the contravariant basis vector, normal to the coordinate line η^α=const.

The covariant components of $\underline{\underline{U}}_s$ are the metrics coefficients $g_{\alpha\beta}$, the mixed components are δ_α^β and the contravariant components are defined by:

$$g^{\alpha\beta} = \underline{g}^\alpha \cdot \underline{g}^\beta$$

or equivalently, by:

$$g^{\alpha\varepsilon} g_{\varepsilon\beta} = \delta_\alpha^\beta$$

$$\underline{g}_\alpha \cdot \underline{g}^\beta = \delta_\alpha^\beta$$

so that:

$$g^{\alpha\alpha} = \frac{g_{\beta\beta}}{g} \qquad (\alpha \neq \beta)$$

$$g^{\alpha\beta} = -\frac{g_{\alpha\beta}}{g} \qquad \det(g^{\alpha\beta}) = \frac{1}{g}$$

The surface gradient $\underline{\nabla}_s$ is expressed in terms of the dual basis vectors as:

$$\underline{\nabla}_s = \frac{\partial}{\partial \underline{r}_0} = \underline{g}^\alpha \frac{\partial}{\partial \eta^\alpha}$$

2.3.4 Curvature tensor. Second fundamental form.

The unit normal n to S at P_s is defined by:

$$\underline{n} = \frac{\underline{g}_1 \wedge \underline{g}_2}{\sqrt{g}} = \frac{1}{\sqrt{g}} \frac{\partial y_0^i}{\partial \eta^1} \frac{\partial y_0^j}{\partial \eta^2} (\underline{c}_i \wedge \underline{c}_j)$$

The elementary vector dn lyies in the tangent plane of S at P_s

$$\underline{g}_\alpha \cdot d\underline{n} = 0 \qquad \underline{g}^\alpha \cdot d\underline{n} = 0$$

The surface gradient of n is the second fundamental tensor of S also referred to as (normal) curvature tensor $\underline{\underline{K}}$:

$$\underline{\underline{K}} = \underline{\nabla}_s \underline{n} = \frac{\partial \underline{n}}{\partial \underline{r}_0} = \underline{g}^\alpha \frac{\partial \underline{n}}{\partial \eta^\alpha} \qquad (2.3)$$

The tensor $\underline{\underline{K}}$ is symmetric:

$$\underline{g}^\alpha \frac{\partial \underline{n}}{\partial \eta^\alpha} = \frac{\partial \underline{n}}{\partial \eta^\alpha} \underline{g}^\alpha$$

and non definite.

Its covariant components $K_{\alpha\beta}$ define the second fundamental form $q_2(S)$ of S which is the scalar invariant of the two elementary vectors dn and dr_0

$$q_2(S) = d\underline{r}_0 \cdot d\underline{n} = \frac{\partial \underline{r}_0}{\partial \eta^\alpha} \cdot \frac{\partial \underline{n}}{\partial \eta^\beta}\, d\eta^\alpha\, d\eta^\beta = \qquad (2.4)$$

$$= \underline{a}_\alpha \cdot \underline{\nabla}_s \underline{n} \cdot \underline{a}_\beta = K_{\alpha\beta}\, d\eta^\alpha\, d\eta^\beta$$

The two principal invariants of $\underline{\underline{K}}$, denoted by K and K_T respectively, are:

$$K = T_r(\underline{\underline{K}}) = K^\alpha_\alpha$$

$$K_T = \det(K^\beta_\alpha)$$

2K is the mean (normal) curvature of S at P_S and K_T is the total, or Gaussian, curvature of S at P_S.

The total curvature K_T can be expressed in terms of only the coefficients of the metrics and their derivatives (Theorema egregium of Gauss). It is thus an intrinsec property invariant with respect to bending of S.

Upon the symmetry of $\underline{\underline{K}}$ there follows that $\underline{\underline{K}}$ can be put in a diagonal form.

At each regular point P_s of S there exist at least two orthogonal directions with respect to which the curvature tensor is diagonal. These directions are called principal directions of $\underline{\underline{K}}$. The corresponding eigenvalues are called principal curvatures and lines whose tangent vector coincide with a principal direction are called lines of curvature.

2.3.5 Covariant derivation on S.

The surface gradient $\underline{\nabla}_s \underline{F}_s$ of a surface vector $\mathbf{F}_s$ is not a tangential tensor as it has non zero right normal component.
Indeed, from $\underline{F}_s \cdot \underline{n} = 0$ it follows that:

$$0 = \underline{\nabla}_s (\underline{F}_s \cdot \underline{n}) = (\underline{\nabla}_s \underline{F}_s) \cdot \underline{n} + \underline{F}_s \cdot \underline{\nabla}_s \underline{n}$$

so that on account of eqn (2.3):

$$(\underline{\nabla}_s \underline{F}_s) \cdot \underline{n} = -\underline{F}_s \cdot \underline{\underline{K}} \qquad (2.5)$$

Hence:

$$\underline{\nabla}_s \underline{F}_s = (\underline{\nabla}_s \underline{F}_s) \cdot \underline{\underline{U}}_s - \underline{F}_s \cdot \underline{\underline{K}}\ \underline{n}$$

where the first contribution on the r.h.s. is a surface tensor.

It is similarly proved that the surface gradient $\underline{\nabla}_s \underline{\underline{T}}_s$ of a surface tensor $\underline{\underline{T}}_s$ is not a tangential (third order) tensor and one has:

$$\underline{\nabla}_s \underline{\underline{T}}_s = (\underline{\nabla}_s \underline{\underline{T}}_s) \cdot \underline{\underline{U}}_s - \underline{\underline{K}} \cdot \tilde{\underline{\underline{T}}}_s\ \underline{n} = (\underline{\nabla}_s \underline{\underline{T}}_s)_s - \underline{\underline{K}} \cdot \tilde{\underline{\underline{T}}}_s\ \underline{n}$$

where $\tilde{\underline{\underline{T}}}_s$ is the transposed of $\underline{\underline{T}}_s$.
The simplified notation for $(\underline{\nabla}_s \underline{\underline{T}}_s)_s$ has been used since $\underline{\nabla}_s \underline{\underline{T}}_s$ has no left normal component ($\underline{n} \cdot \underline{\nabla}_s$ =0).

The usual derivatives of surface vectors (tensors) or of their scalar components do not have tensorial character in view of the fact that:

a) the coordinate base vectors are not constant;

b) their surface gradients do not have tensorial character.

The covariant derivatives denoted with a slant ovviates these shortcomings. Loosely speaking, the basis vectors behave as "constant" vector with respect to covariant differentiation and the covariant derivatives have tensorial character.
Thus, one has, for the surface part of the surface gradient of $\mathbf{F}_S$:

$$(\underline{\nabla}_s \underline{F}_s) \cdot \underline{\underline{U}}_s = \underline{g}^{\alpha} \underline{F}_{s/\alpha} = \underline{g}^{\alpha} F^{\beta}_{/\alpha} \underline{g}_{\beta} = \underline{g}^{\alpha} \bar{F}_{\beta/\alpha} \underline{g}^{\beta}$$

where $F^{\beta}_{/\alpha}$ and $\bar{F}_{\beta/\alpha}$ are the mixed and covariant components of $(\underline{\nabla}_s \underline{F}_s)_s$ defined by:

$$F^{\beta}_{/\alpha} = \frac{\partial F^{\beta}}{\partial \eta^{\alpha}} + F^{\varepsilon} \gamma^{\beta}_{\varepsilon\alpha}$$

$$F_{\beta/\alpha} = \frac{\partial F_{\beta}}{\partial \eta^{\alpha}} - F_{\varepsilon} \gamma^{\varepsilon}_{\alpha\beta}$$

$$\underline{F}_{s/\alpha} = \frac{\partial}{\partial \eta^{\alpha}} \left(F^{\beta} \underline{g}_{\beta} \right) = \frac{\partial}{\partial \eta^{\alpha}} \left(F_{\beta} \underline{g}^{\beta} \right)$$

As this latter equation shows, the "non-tensorial" character of $\frac{\partial F^{\beta}}{\partial \eta^{\alpha}}$ is "balanced" by the " non-tensorial character" of $F^{\beta} \frac{\partial \underline{g}_{\beta}}{\partial \eta^{\alpha}}$.

2.3.6 Surface gradient of basis vectors. Crystoffel symbols.

According to eqn (2.5) it is:

$$\underline{\nabla}_s \underline{g}_{\alpha} = (\underline{\nabla}_s \underline{g}_{\alpha})_s - \underline{g}_{\alpha} \cdot \underline{K}\, \underline{n}$$

where:

$$(\underline{\nabla}_s \underline{g}_{\alpha})_s = \left(\underline{g}^{\beta} \frac{\partial \underline{g}_{\alpha}}{\partial \eta^{\beta}} \right) \cdot \underline{\underline{U}}_s = \underline{g}^{\beta} \frac{\partial \underline{g}_{\alpha}}{\partial \eta^{\beta}} \cdot \underline{g}^{\varepsilon} \underline{g}_{\varepsilon} = \underline{g}^{\beta} \gamma^{\varepsilon}_{\alpha\beta} \underline{g}_{\varepsilon}$$

The quantities defined by:

$$\gamma^{\varepsilon}_{\alpha\beta} = \frac{\partial \underline{g}_{\alpha}}{\partial \eta^{\beta}} \cdot \underline{g}^{\varepsilon} \qquad \gamma_{\alpha\beta,\varepsilon} = \frac{\partial \underline{g}_{\alpha}}{\partial \eta^{\beta}} \cdot \underline{g}_{\varepsilon}$$

are called, respectively, Crystoffel symbols of the second and first type.

They are not the components of a third order tensor, and their transformation formula under a change of coordinate is readily deduced by their definition, written, for instance, as:

$$\gamma_{\alpha\beta,\varepsilon} = \frac{\partial^2 \underline{r}_0}{\partial \eta^{\alpha} \partial \eta^{\beta}} \cdot \frac{\partial \underline{r}_0}{\partial \eta^{\varepsilon}}$$

The Crystoffel symbols are symmetric with respect to the indices and can be expressed in terms of derivatives of the metric coefficients as:

$$\gamma_{\alpha\beta,\varepsilon} = \frac{1}{2} \left[\frac{\partial g_{\alpha\varepsilon}}{\partial \eta^{\beta}} + \frac{\partial g_{\beta\varepsilon}}{\partial \eta^{\alpha}} - \frac{\partial g_{\alpha\beta}}{\partial \eta^{\varepsilon}} \right]$$

$$\gamma^{\varepsilon}_{\alpha\beta} = g^{\varepsilon\delta} \gamma_{\delta\beta,\alpha}$$

so that are intrinsec properties of S.

Components of derivatives of contravariant base vectors are given by:

$$\frac{\partial \underline{g}^{\alpha}}{\partial \eta^{\beta}} \cdot \underline{g}_{\varepsilon} = - \gamma^{\alpha}_{\varepsilon\beta}$$

$$\frac{\partial \underline{g}^{\alpha}}{\partial \eta^{\beta}} \cdot \underline{g}^{\varepsilon} = - \gamma^{\alpha}_{\beta\delta} g^{\delta\varepsilon}$$

2.3.7 Normal and geodesic curvatures

Let $\mathcal{C}(t)$ be an arbitrary regular curve on S,

$$\eta^{\alpha} = \eta^{\alpha}(t) \qquad t \in [t_0, t_1]$$

its parametric representation, $\underline{\lambda}$ its tangent unit vector and ds its elementary arc length.

$$\underline{\lambda} = \frac{d\underline{r}_0}{ds} = \lambda^{\alpha}\underline{G}_{\alpha} \qquad \lambda^{\alpha} = \frac{d\eta^{\alpha}}{ds}$$

$$\frac{ds}{dt} = \sqrt{g_{\alpha\beta}\,\dot{\eta}^{\alpha}\dot{\eta}^{\beta}} \qquad \dot{\eta}^{\alpha} = \frac{d\eta^{\alpha}}{dt}$$

The rate of change in the direction of the unit vector $\underline{\lambda}$ (directional derivative) is given by:

$$\frac{d}{ds} = \underline{\lambda}\cdot\underline{\nabla}_s = \lambda^{\alpha}\frac{\partial}{\partial\eta^{\alpha}}$$

The surface gradient of the unit vector $\underline{\lambda}$ is given, according to equation (15) by:

$$\underline{\nabla}_s\,\underline{\lambda} = (\underline{\nabla}_s\,\underline{\lambda})\cdot\underline{\underline{U}}_s - \underline{\lambda}\cdot\underline{\underline{K}}\,\underline{n}$$

Let N(t) be the principal normal to $\mathcal{C}(t)$ and (1/R) its curvature, positive if $\mathcal{C}(t)$ is convex. Then:

$$-\frac{\underline{N}}{R} = \frac{d\underline{\lambda}}{ds} = \underline{\lambda}\cdot\underline{\nabla}_s\,\underline{\lambda} = (\underline{\lambda}\cdot\underline{\nabla}_s\,\lambda)\cdot\underline{\underline{U}}_s - \underline{\lambda}\cdot\underline{\underline{K}}\cdot\underline{\lambda}\;\underline{n}$$

Thus, in general, the principal normal of the surface curve $\mathcal{C}(t)$ at P_S has tangential component. It follows that the osculating plane of $\mathcal{C}(t)$ at P_S is normal to the tangent plane of S at P_S but does not contain, in general, the unit normal **n**.

Let ϑ be the angle between the osculating plane and the normal plane so that:

$$\cos\vartheta(P_s) = \underline{N}(P_s)\cdot\underline{n}(P_s)$$

The normal and tangential projections of (-N/R) are called, respectively, normal (K_n) and geodesic (K_g) curvatures of .
They are given by:

$$K_n = \frac{\cos\vartheta}{R} = \underline{\lambda}\cdot\underline{\underline{K}}\cdot\underline{\lambda}$$

$$K_g = \frac{\sin\vartheta}{R} = \left|(\underline{\lambda}\cdot\underline{\nabla}_s\,\underline{\lambda})\cdot\underline{\underline{U}}_s\right| = \left|\lambda^{\alpha}\,\underline{\lambda}_{/\alpha}\right|$$

The normal curvature K_n is equal to the inverse ratio of the first two fundamental forms of S:

$$K_n = \underline{\lambda}\cdot\underline{\underline{K}}\cdot\underline{\lambda} = \lambda^{\alpha}K_{\alpha\beta}\lambda^{\beta} = \frac{d\eta^{\alpha}}{ds}K_{\alpha\beta}\frac{d\eta^{\beta}}{ds} =$$
$$= \frac{K_{\alpha\beta}\,d\eta^{\alpha}d\eta^{\beta}}{g_{\alpha\beta}\,d\eta^{\alpha}d\eta^{\beta}}$$

If K_1 and K_2 denote the two principal curvatures of S at P_S it is(unless inessential change of suffixes):

$$|K_1| \leq |K_n| \leq |K_2|$$

2.4 Kinematics of surface phase

The velocity $\underline{W}$ of a point on S is defined by:

$$\underline{W} = \frac{\partial \underline{r}_o(\eta^\alpha, t)}{\partial t} \qquad (2.6)$$

and its cartesian components by:

$$W_i = \frac{\partial y_{oi}}{\partial t}$$

Notice that the algebraic representation of S defines only the normal componet of the velocity W. Indeed from the differential of equation $F(y_{oi}, t) = 0$:

$$\underline{W} \cdot \underline{\nabla} F + \frac{\partial F}{\partial t} = 0$$

and the definition of the unit normal

$$\underline{n} = \underline{\nabla} F / |\underline{\nabla} F|$$

one obtains:

$$\underline{W} \cdot \underline{n} = - \frac{1}{|\underline{\nabla} F|} \frac{\partial F}{\partial t} \qquad (2.7)$$

2.5 Examples

To further elaborate about the geometry and kinematics of we shall consider two examples that are typical of situations of interest for the present lectures insofar as they are related to axisymmetric floating zones and drops.
We adopt the synthetic notation:

$$\underline{r}_o = [z_1, z_2, z_3] \ ; \quad \underline{F} = [F_{z_1}, F_{z_2}, F_{z_3}]$$

to represent the cartesian component of $\underline{r}_o$ and of any ve ctor $\underline{F}$.

Example 1

The parametric equation:

$$\underline{r}_o = \left[R(\eta^2, t) \cos \eta^1 \ ; \ R(\eta^2, t) \sin \eta^1 \ ; \ f(\eta^2, t) \right] \quad (2.8)$$

where R and f are real functions, represents, at all times t, a surface of revolution with axis z_3.
Its algebraic representation is:

$$\bar{F}(z_i, t) = z_1^2 + z_2^2 - R^2 \left[g(z_3, t), t \right] = 0 \qquad (2.9)$$

where $\eta^2 = g(z_3, t)$ is the inverse of the function $z_3 = f(\eta^2, t)$.
The surface is bounded by the two circles:

$$z_1^2 + z_2^2 = R^2 \left[g(0, t), t \right] \qquad (R_o^2)$$

$$z_1^2 + z_2^2 = R^2 \left[g(\ell, t), t \right] \qquad (R_\ell^2)$$

where the values in parenthesis apply if the floating zone is anchored, at the two extremities, to two discs of arbitrary radius R_o and R_ℓ respectively. The shape of the floating zone in the meridian plane is given by the curve:

$$\underline{r}_o = \left[R(\eta^2, t) \ ; \ 0 \ ; \ f(\eta^2, t) \right] \qquad \pm z_1 = R \left[g(z_3, t), t \right]$$

We denote with dots partial derivation with respect to time and with an apex partial derivation with respect to η^1.
The coordinate vectors are given by:

$$\underline{G}_1 = \left[-R\sin\eta^1, R\cos\eta^1, 0 \right] = \frac{\partial \underline{r}_0}{\partial \eta^1}$$

$$\underline{G}_2 = \left[R'\cos\eta^1, R'\sin\eta^1, \rho' \right] = \frac{\partial \underline{r}_0}{\partial \eta^2}$$

so that the coefficients of the metrics are:

$$g_{11} = R^2 = h_{10}^2 \quad ; \qquad g_{12} = 0 \qquad ; \qquad g_{22} = R'^2 + \rho'^2 = h_{20}^2$$

Hence the coordinate curves are orthogonal.
The unit normal $\underline{n} = (\underline{G}_1 \wedge \underline{G}_2) / (h_{10} h_{20})$
To determine the coefficients of the second fundamental form one needs the second derivatives of . They are:

$$\underline{n} = \left[\rho'\cos\eta^1 \, ; \, \rho'\sin\eta^1 \, ; -R' \right] \frac{1}{\sqrt{R'^2 + \rho'^2}}$$

$$\frac{\partial^2 \underline{r}_0}{\partial \eta^{1^2}} = \frac{\partial \underline{G}_1}{\partial \eta^1} = \left[-\cos\eta^1, -\sin\eta^1, 0 \right] R$$

$$\frac{\partial^2 \underline{r}_0}{\partial \eta^1 \partial \eta^2} = \frac{\partial \underline{G}_1}{\partial \eta^2} = \left[-\sin\eta^1, \cos\eta^1, 0 \right] R'$$

$$\frac{\partial^2 \underline{r}_0}{(\partial \eta^2)^2} = \frac{\partial \underline{G}_2}{\partial \eta^2} = \left[R''\cos\eta^1, R''\sin\eta^1, \rho'' \right]$$

Hence:

$$b_{11} = -\frac{\rho' R}{\sqrt{R'^2 + \rho'^2}} \quad ; \quad b_{12} = 0 \quad ; \quad b_{22} = \frac{\rho' R'' - \rho'' R'}{\sqrt{R'^2 + \rho'^2}}$$

Thus the coordinate curves are lines of curvature ($g_{12} = b_{12} = 0$).
The principal curvatures are:

$$K_1 = -\frac{b_{11}}{g_{11}} = \frac{\rho'}{R\sqrt{R'^2 + \rho'^2}}$$

$$K_2 = -\frac{b_{22}}{g_{22}} = \frac{\rho'' R' - \rho' R''}{(R'^2 + \rho'^2)^{3/2}}$$

Let $R(\eta^1) = R\,\ell(z_3) \; ; \; \frac{d}{dz_3} = \frac{1}{\rho'} \frac{d}{d\eta^1}$

$$R\,\ell_{z_3} = \frac{R'}{\rho'} \quad ; \quad R\,\ell_{z_3 z_3} = \frac{R''\rho' - R'\rho''}{\rho'^3}$$

$$K_1 = \frac{1}{R\ell\sqrt{R^2 \ell_{z_3}^2 + 1}} \qquad ; \qquad K_2 = -\frac{R\,\ell_{z_3 z_3}}{\left(R^2 \ell_{z_3}^2 + 1\right)^{3/2}}$$

The velocity $\underline{W}$ is:

$$\underline{W} = \frac{\partial \underline{r}_0}{\partial t} = \left[\dot{R}\cos\eta^1 \, ; \, \dot{R}\sin\eta^1, \dot{\rho} \right]$$

and its normal component is:

$$W_n = \underline{W} \cdot \underline{n} = \frac{\rho' \dot{R} - \dot{\rho} R'}{\sqrt{R'^2 + \rho'^2}} \qquad (2.10)$$

Consider now the algebraic representation

It is:

$$\underline{\nabla} F = 2\left[z_1, z_2, -RR'\frac{\partial g}{\partial z_3}\right]$$

$$\frac{\partial F}{\partial t} = -2R\left[\dot R + R'\dot g\right]$$

$$|\underline{\nabla} F| = 2R\left[1 + \left(R'\frac{\partial g}{\partial z_3}\right)^2\right]^{1/2}$$

$$W_n = \left(\dot R + R'\dot g\right) \Big/ \sqrt{1 + \left(R'\frac{\partial g}{\partial z_3}\right)^2}$$

It is readily checked that the expression of the normal component W_n of W as computed from equation (2.7) coincides with the expression given by equation (2.10) when one accounts for the fact that:

$$z_3 = f(\eta^2, t) \quad ; \quad \eta^2 = g(z_3, t)$$

$$\frac{\partial g}{\partial z_3} = \frac{1}{f'} \quad ; \quad \dot g = -\frac{\dot f}{f'}$$

Example 2

The parametric equation:

$$\underline{r}_0 = \left[A(t)\cos\eta^2\cos\eta^1 \ ; \ B(t)\cos\eta^2\sin\eta^1 \ ; \ C(t)\sin\eta^2\right] \qquad (2.11)$$

with A, B, C real function describes, for all time t, an ellipsoid with semi-axes A, B, C as evidenced by the corresponding algebraic equation:

$$F(z_i, t) = \frac{z_1^2}{A^2(t)} + \frac{z_2^2}{B^2(t)} + \frac{z_3^2}{C^2(t)} - 1 = 0 \qquad (2.12)$$

When the following inequality is imposed:

$$C(t) \geq C(t)\sin\eta^2 \geq const = Z_{30}$$

the surface (2.11) is part of an ellipsoid bounded by the ellips obtained from (2.12) for $Z_3 = Z_{30}$ or, in parametric form, from (2.11) for $C(t)\sin^2\eta^2 = Z_{30}$ and $\cos\eta^2 = \sqrt{1-(Z_{30}/C(t))^2}$

For A = B = C the surface is spherical.

Proceeding as before, one obtains for the metrics coefficients:

$$g_{11} = \cos^2\eta^2\left(A^2\sin^2\eta^1 + B^2\cos^2\eta^1\right)$$

$$g_{12} = \left(A^2 - B^2\right)\sin 2\eta^2 \sin 2\eta^1 / 4$$

$$g_{22} = \left(A^2\cos^2\eta^1 + B^2\sin^2\eta^1\right)\sin^2\eta^2 + C^2\cos^2\eta^2$$

The unit normal is given by

$$\underline{n} = \frac{1}{\sqrt{g}}\left[BC\cos^2\eta^2\cdot\cos\eta^1 \ ; \ AC\cos^2\eta^2\sin\eta^1 \ ; \ \frac{AB}{2}\sin 2\eta^2\right]$$

Finally, the coefficients of the second fundamental form are given by:

$$\sqrt{g}\ b_{11} = -ACB\cos^3\eta^2$$

$$\sqrt{g}\ b_{12} = 0$$

$$\sqrt{g}\ b_{22} = -ACB\cos\eta^2$$

The coordinate curves are not orthogonal ($g_{12} \neq 0$) unless A(t) = B(t) (ellipsoids of revolution with axis z_3). When they are, they are also lines of curvature since the second fundamental form is always diagonal.

The normal curvatures in the direction of the coordinate curves are:

$$K_1 = -\frac{b_{11}}{g_{11}} = \frac{ABC\cos^3\eta^2}{\sqrt{g}\;g_{11}}$$

$$K_2 = -\frac{b_{22}}{g_{22}} = \frac{ABC\cos\eta^2}{\sqrt{g}\;g_{22}}$$

The total curvature is computed from the relation $K_T = b/g$. The mean curvature ($K/2$) from the definition of K.

The results are:

$$K_T = \frac{A^2B^2C^2\cos^4\eta^2}{g^2}$$

$$K = \frac{ABC\cos\eta^2\left[\cos^2\eta^2\,g_{22} + g_{11}\right]}{\sqrt{g}\;g_{11}\,g_{22}}$$

For spherical surfaces (A = B = C = R) one recovers the well known expression $K_T = R^{-2}$; $K = \frac{2}{R}$.

The velocity $\underline{W}$ is

$$\underline{W} = \left[\dot{A}\cos\eta^2\cos\eta^1 ; \dot{B}\cos\eta^2\sin\eta^1 ; \dot{C}\sin\eta^2\right]$$

3. SURFACES EQUILIBRIUM THERMODYNAMICS

3.1 Energy fundametal relation. Euler, Gibbs and Gibbs-Duhem equations

We assume that a local formulation of the surface-phase equilibrium thermodynamics applies.

There is evidence of the applicability of this assumption in many instances but its true range of validity still needs to be accurately characterized and adequately defined.

The development of a theory based on the local formulation and comparison of its results with either experimental finding or results from statistical approaches will help assessing this.

We shall follow a postulatory approach quite analogous to the one well established for volume phases.

We postulate that an equilibrium thermodynamic state of the surface phase is defined by the set of extensive variables $\{\mathcal{S}, \Omega, X_i\}$ where $\mathcal{S}$ is the entropy, Ω the area and X_i are all other variables needed to uniquely characterize it. The question of the number and nature of the X_i will be taken up later on, when dealing with specific cases. Suffice here to mention that they may be masses, entropies, electric polarization vectors. We further postulate the existence of an energy fundametal relation:

$$\mathcal{U} = \mathcal{U}(\mathcal{S}, \Omega, X_i) \qquad (3.1)$$

expressing the internal energy $\mathcal{U}$ as a first order homogeneous and at least twice differentiable function of the basic set of extensive variables.

Let:

$$\tilde{T} = \frac{\partial \mathcal{U}}{\partial \mathcal{S}} ; \quad \sigma = \frac{\partial \mathcal{U}}{\partial \Omega} ; \quad \tilde{y}_i = \frac{\partial \mathcal{U}}{\partial X_i} \qquad (3.2)$$

where $\tilde{T}$ is the absolute temperature, σ the (equilibrium) surface tension and $\tilde{y}_i$ denotes the intensive parameter conjugated to X_i in the energy representation (3.1).

Extensive quantities per unit of surface (surface densities) will be denoted with the corresponding tilded low case latters. Low case letters with a bar will denote quantities per unit mass (referred to as specific quantities). The only exception to this notation is for the mass surface density which will be denoted by $\tilde{\rho}$. The area per unit mass is $\bar{\omega}$ and the following relations hold:

$$\tilde{\rho}\,\bar{\omega} = 1 \quad ; \quad \tilde{x}_i = \tilde{\rho}\,\bar{x}_i$$

The couples ($\tilde{T}$, $\bar{s}$), (σ, $\bar{\omega}$), ($\tilde{y}_i$, $\bar{x}_i$) will referred to as couples conjugated with respect to the energy representation. From the postulated first order homogenity of the energy fundamental relation there follow the Euler, Gibbs and Gibb-Duhem relations:

$$\begin{aligned} \mathcal{U} &= \tilde{T}\mathcal{S} + \sigma\Omega + \sum_i \tilde{y}_i X_i \\ d\mathcal{U} &= \tilde{T}\,d\mathcal{S} + \sigma\,d\Omega + \sum_i \tilde{y}_i\,dX_i \qquad (3.4) \\ 0 &= \mathcal{S}\,d\tilde{T} + \Omega\,d\sigma + \sum_i X_i\,d\tilde{y}_i \end{aligned}$$

wherein, if X_j denote the mass of the j-th constituent and $\mathcal{M}$ the total mass of the surface phase it is:

$$\mathcal{M} = \sum_j X_j \quad ; \quad 1 = \sum_j \bar{x}_j \quad ; \quad \tilde{\rho} = \sum_j \tilde{x}_j \qquad (3.5)$$

Analogous relations are readily established in terms of surface densities or specific quantities.
In the absence of phase changes, the number of intensive degrees of freedom equals (upon the Gibbs-Duhem equation)

that of specific degrees of freedom. The equilibrium thermodynamic description of the surface is completely characterized by the energy fundamental relation (or by the fundamental relation in terms of other thermodynamic potentials, see later on) or by as many independent equations of state as it is the number of thermodynamic degrees of freedom (equilibrium constitutive equations).

3.2 Thermodynamic Stability

When the thermodynamic state of the surface-phase can be described in terms of local variables associated with the surface-phase alone one may speak of its (intrinsec) thermodynamic stability.
This, in turn, can be related to the condition that $d^2\bar{u} > 0$ in the absence of phase changes within the layer.

Thus thermodynamic stability implies that the Hessian of the function $\bar{u} = \bar{u}(\bar{s}, \bar{\omega}, \lambda_i)$ be positive definite. As known, this is equivalent to the two following stability rules:

I) The derivation of any intensive parameter with respect to its conjugate (specific) extensive variable is certainly positive if no combination of conjugated variables is held constant

II) For thermodynamic derivatives of the above type replacing an extensive parameter held constant with its conjugated intensive parameter never increases the (posivite) value of the derivative.

As detailed when dealing with specific cases, stability with respect to entropy variations leads to the notion of surface specific heat coefficients, stability with respect to area variations leads to the notion of surface compressibility coefficients and so on, for the other types of stability. The second stability rule established important inequalities within the sets of the above mentioned coefficients.

3.3 Thermodynamic potentials

Thermodynamics potentials are defined as partial Legendre transforms of the internal energy.

Their natural variables include a number of intensive parameters and thus they are first order homogeneous functions only of the remaining extensive variables.
Stability conditions are sufficient conditions for the admissibility of the Legendre transforms.
To simplify the notation, the internal energy is represented as

$$\mathcal{U} = \sum_k \tilde{y}_k X_k = \mathcal{U}(X_k) \qquad (3.6)$$

(where the X_k now include $\mathcal{S}$ and Ω).
The partial Legendre transform of $\mathcal{U}$ with respect to its first variables is the thermodynamic potential P_q whose natural variables are the set

$$(\tilde{y}_1, \ldots, \tilde{y}_q, {}_{q+1} \ldots, X_n)$$

Upon the properties of the Legendre transforms it follows that:

$$\begin{aligned} P_q &= \mathcal{U} - \sum_{k=1}^{q} \tilde{y}_k X_k = \sum_{k=q+1}^{n} \tilde{y}_k X_k \\ dP_q &= -\sum_{k=1}^{q} X_k \, d\tilde{y}_k + \sum_{k=q+1}^{n} \tilde{y}_k \, dX_k \end{aligned} \qquad (3.7)$$

In the first equation, the first equality defines P_q and the second equality gives the Euler representation of P_q . The second equation is the Gibbs equation for P_q . The Gibbs-Duhem equation is clearly the same.
The possibility of expressing P_q as functions of its intensive natural variables relies on the possibility of solving for ($X_1, \ldots$ $\ldots, X_q$) the (3.7) equations of state:

As known, this is possible when the Jacobian of the $\tilde{y}_j$ with respect to $X_j\ (1 \leq j \leq q)$ is different from zero. Hence, as anticipated, thermodynamic stability (which ensures that this Jacobian is positive) is a sufficient condition for the definition of $\tilde{P}_k$.

Three noteworthy examples of thermodynamic potentials will now be given:

1) The Helmotz free energy F

F is the first order Legendre transform of $\mathcal{U}$ with respect to $\mathcal{S}$ and one has:

$$F = \mathcal{U} - \tilde{T}\mathcal{S} = \sigma\Omega + \sum \tilde{y}_i X_i = F(\tilde{T}, \Omega, X_i)$$

$$dF = -\mathcal{S}\, d\tilde{T} + \sigma\, d\Omega + \sum \tilde{y}_i\, dX_i \tag{3.8}$$

It follows that, when the state of the surface is sufficiently characterized only by $\mathcal{S}$ and Ω , one has $F = \sigma\Omega$, i.e. the surface tension can be interpreted as the Helmotz free energy per unit area (see later on for the more general definition of as a thermodynamic potential).

2) The surface enthalpy H

It is a first order Legendre transform of $\mathcal{U}$ with respect to the surface area Ω .

Thus:

$$H = \mathcal{U} - \sigma\Omega = \tilde{T}\mathcal{S} + \sum \tilde{y}_i X_i = H(\mathcal{S}, \sigma, X_i)$$

$$dH = \tilde{T}\, d\mathcal{S} - \Omega\, d\sigma + \sum \tilde{y}_i\, dX_i \tag{3.9}$$

The potential H plays, in surface thermodynamics, the same role played by the enthalpy (hence the name) in volume thermodynamics.

3) The grand potential $\mathfrak{J}$

It is the total Legendre transform of $\mathcal{U}$ with respect to all variables other than Ω .

Thus:

$$\mathfrak{J} = \mathcal{U} - \tilde{T}\mathcal{S} - \sum \tilde{y}_i X_i = \sigma\Omega = \mathfrak{J}(\tilde{T}, \Omega, \tilde{y}_i)$$

$$d\mathfrak{J} = -\mathcal{S}\, d\tilde{T} + \sigma\, d\Omega - \sum X_i\, d\tilde{y}_i \tag{3.10}$$

Hence, in the general case, the surface tension can be interpreted as the surface density of the grand potential. Obviously, this defintion reduces to the one previously given since, in that case, the grand potential coincides with the Helmotz free energy.

4.UNCHARGED AND UNPOLARIZED LAYERS

The internal energy natural variables are the entropy, the area and the masses of the constituents.
The corresponding surface densities are denoted by $\tilde{s}$ and $\tilde{\rho}_j$, respectively.
The specific quantities by $\bar{s}$, $\bar{\omega}$ and $\bar{c}_j$ respectively.
The surface density of total mass is denoted by $\tilde{\rho}$. It is $(\text{for } \tilde{\rho} \neq 0)$:

$$\tilde{\rho} = \sum_j \tilde{\rho}_j \ ; \qquad \tilde{\rho}\,\bar{\omega} = 1 \ ; \qquad \tilde{s} = \tilde{\rho}\,\bar{s}$$
$$\tilde{\rho}_j = \tilde{\rho}\,\bar{c}_j \ ; \qquad \bar{c}_j = \bar{\omega}\,\tilde{\rho}_j \ ; \qquad \sum_j \bar{c}_j = 1 \qquad (4.1)$$

The set of intensive parameters conjugated to the set $\{\bar{s}, \bar{\omega}, \bar{c}_j\}$ will be denoted as $\{\tilde{T}, \sigma, \tilde{\mu}_j\}$ where $\tilde{T}$ is the absolute temperature, σ the equilibrium surface tension and $\tilde{\mu}_j$ the chemical potential per unit mass of species j. The tilde denotes values pertaining to the surface phase which do not necessarily coincide with the values of the adjacent volume phases. The energy fundamental relation is, in terms of quantities per unit mass:

$$\bar{u} = \bar{u}\left(\bar{s}, \bar{\omega}, \bar{c}_j\right) \qquad (4.2)$$

and the corresponding Euler, Gibbs and Gibbs-Duhem equations read:

$$\bar{u} = \tilde{T}\bar{s} + \sigma\bar{\omega} + \sum_j \tilde{\mu}_j \bar{c}_j$$
$$d\bar{u} = \tilde{T}d\bar{s} + \sigma d\bar{\omega} + \sum_j \tilde{\mu}_j\, d\bar{c}_j \qquad (4.3)$$
$$0 = \bar{s}\,d\tilde{T} + \bar{\omega}\,d\sigma + \sum_j \bar{c}_j\, d\tilde{\mu}_j$$

with $\sum_j d\bar{c}_j = 0$.
In terms of surface densities the Gibbs-Duhem relation reads:

$$d\sigma = -\tilde{s}\,d\tilde{T} - \sum_j \tilde{\rho}_j\, d\tilde{\mu}_j \qquad (4.4)$$

This relation can be looked upon as a generalization of the Gibbs adsorption equation if the surface densities are interpreted as "excess" values.
Surface thermodynamic potentials may be defined as described in paragraph (3.3).
Of particular interest in fluid problems is, as known, the enthalpy. We shall thus introduce a surface specific enthalpy defined by:

$$\bar{h} = \bar{h}\left(\bar{s}, \sigma, \bar{c}_j\right) = \bar{u} - \sigma\bar{\omega} = \tilde{T}\bar{s} + \sum_j \tilde{\mu}_j \bar{c}_j \qquad (4.5)$$

where the last equality provides the Euler relation for $\bar{h}$ and in the first equality the natural variables of $\bar{h}$ are shown.
The Gibbs' relation for $\bar{h}$ reads:

$$d\bar{h} = \tilde{T}\,d\bar{s} - \bar{\omega}\,d\sigma + \sum_j \tilde{\mu}_j\, d\bar{c}_j \qquad (4.6)$$

Thermodynamic stability entails the positive definite character of the Hessian of the specific internal energy $\bar{u}$.
In particular, the frozen specific heat and "compressibility" coefficients are essentially positive quantities defined by:

$$\frac{\tilde{T}}{C_\omega} = \left(\frac{\partial \tilde{T}}{\partial \bar{s}}\right)_{\bar{\omega}, \bar{c}_j} \ ; \qquad \frac{\tilde{T}}{C_\sigma} = \left(\frac{\partial \tilde{T}}{\partial \bar{s}}\right)_{\sigma, \bar{c}_j}$$
$$\frac{K_s}{\bar{\omega}} = \left(\frac{\partial \sigma}{\partial \bar{\omega}}\right)_{\bar{s}, \bar{c}_j} \ ; \qquad \frac{K_T}{C_\omega} = \left(\frac{\partial \sigma}{\partial \bar{\omega}}\right)_{T, \bar{c}_j} \qquad (4.7)$$

where C_ω (C_σ) is the surface specific heat coefficient at constant area (tension) and K_s (K_T) is the isentropic (isotherm) surface compressibility coefficient. The specific heat coefficients have the dimension of a surface tension.

Gibbs' definition of an elasticity coefficient E is usually reported as given by:

$$E = \frac{d\sigma}{d\ln\Omega} = \Omega\,\frac{d\sigma}{d\Omega}$$

where Ω is the total area of the surface.

Clearly this way of writing is formally incorrect because it does not specify the parameters held constant. Apparently, what is held constant is the temperature and the composition of the surface phase. Hence, upon the first order homogenity of the internal energy $\mathcal{U}$ it follows that $E = K_T$.

Upon the second stability rule it follows that:

$$C_\sigma \geq C_\omega \quad ; \quad K_T \leq K_s \qquad (4.8)$$

Those inequalities are analogous to those holding in volume phases (C_σ is the surface equivalent of the specific heat at constant pressure and C_ω is the surface equivalent of the specific heat at constant volume).

Other relevant stability inequalities are:

$$\left(\frac{\partial \tilde{\mu}_j}{\partial \tilde{c}_j}\right)_{\tilde{s},\tilde{\omega},\tilde{c}_k/c_j} > 0 \qquad (4.9)$$

Notice finally, that additional specific heat and compressibility coefficients can be defined other than those (4.7) for "frozen" composition.

For instance, when surface chemical reactions occur, coefficients defined for one or more affinities held constant are relevant in the study of the dynamical evolution.

5. THERMODYNAMIC MODELS

Macroscopic thermodynamics defines and describes the properties of the fundamental relations and/or state equations. Their explicit form has to be derived on the basis of statistical thermodynamics or of experiments or through a combination of both. Such explicit forms can also be referred to as thermodynamic models of the surface.

One such model (the simplest one) is the one applyng to the Gibbs surface for single component systems. In this case the location of the dividing surface is such that the excess mass is zero. Then the excess internal energy is function only of the excess entropy and the area. In terms of surface densities the Euler, Gibbs and Gibbs-Duhem equations read:

$$\begin{aligned} \tilde{u} &= \tilde{T}\tilde{s} + \sigma \\ d\tilde{u} &= \tilde{T}\,d\tilde{s} \\ 0 &= \tilde{s}\,d\tilde{T} + d\sigma \end{aligned} \qquad (5.1)$$

The surface has only one specific degree of freedom so that a thermodynamic model is completely characterized (unless inessential constants) when the explicit form of an equation of state is given.

The simplest model mentioned above is defined by a linear dependence of σ upon $\tilde{T}$. Thus the equation of state reads:

$$\sigma = \sigma_r - c\,(\tilde{T} - \tilde{T}_r) \qquad (5.2)$$

where the subscript (r) denotes a reference state and c is a constant whose thermodynamic meaning is readily derived from the Gibbs-Duhem equation.

Indeed: subsequently, upon equations $(5.1)_3$ and (5.2)

$$\tilde{s} = -\frac{d\sigma}{d\tilde{T}} = C$$

Hence $C = \tilde{s}_r$ is the entropy density in the reference state. The expression for the internal energy can be obtained from the Euler equation $(5.1)_4$ and one gets accounting for (5.2) :

$$\tilde{u} = \tilde{T}_r \tilde{s}_r + \sigma_r$$

Hence also the excess density of internal energy is costant.

It appears that this model is somewhat degenerate in so far as the fundamental relation $\tilde{u} = \tilde{u}(\tilde{s})$ reduces to $\tilde{u} = \tilde{u}_r = u(\tilde{s}_r)$ = const and therefore the Gibbs equation in the specific energetic representation is identically satisfied. The degeneracy is also evident from the fact that the specific heat coefficient vanishes (see later on) (neutral stability). Hence the simple model in which σ is locally expressed as a linear function of $\tilde{T}$ must be handled with some care.

Rewriting the (5.2) as:

$$\sigma = A + B\tilde{T}$$

we can say that, since the constant entropy and energy would be positive, it is necessary that A must be positive and B negative. Then the surface tension must be a monitonically decreasing function of the temperature.

Considering that the specific enthalpy must be positive one gets the same conclusion ($B < 0$).

The temperature $\tilde{T}$ is a primitive variable tha cannot be defined as $\frac{\partial \tilde{u}}{\partial \tilde{s}}$.

- The thermodynamic stability conditions for the same reason ($\tilde{u}$ = constant) must be expressed in terms of non constant potentials, like the specific enthalpy. In a way quite analogous to the model of perfect gas (enthalpy linear functions of $\tilde{T}$ and constant specific heat a constant pressure) the constant B can

be interpreted as specific (for unit of area) heat at constant surface tension.
  For the thermodynamic stability this specific heat must be positive, therefore we can conclude that B must necessary be negative.
- Being $\tilde{u}$ constant the specific (in this model the surface phase has no mass) heat at constant area vanishes (this is ., in essence, the degenerate aspect of the model).
- The second stability rule (specific heat at constant surface tension greater or equal than specific heat at constant area) is consequently satisfied (and also this implies that must be B < 0).

In conclusion, assuming a thermodynamic model in which the surface tension depends linearly only on the temperature (system with only one degree of freedom) the thermodynamic stability of such model implies that the surface tension decreases with temperature.

This brings to two consideration of the greatest importance:

- To assume, for this model, that surface tension may increase increasing the temperature, is equivalent to consider that the surface phase is thermodynamically instable.
- One may ask himself if the thermodynamic stability can be garanteed by a non linear dependence of σ from $\tilde{T}$; pratically, the answer is negative because, as indicated by

$$\tilde{h}(\tilde{T}) = -\tilde{T}\,\frac{d\sigma}{d\tilde{T}}$$

generally (id est for every explicit expression of $\sigma(\tilde{T})$)

$$C_\sigma = -\frac{d\sigma}{d\tilde{T}} - \tilde{T}\,\frac{d^2\sigma}{d\tilde{T}^2}$$

and it is irrealistic to suppose that C_σ is positive in a finite range of temperatures (it would be necessary that $d^2\tilde{\sigma}/d\tilde{T}^2$ was negative and greater, in module, than $\frac{1}{T}\frac{d\sigma}{dT}$)

- All these conclusions are not in contraddiction with many experimental results that show for $\sigma(\tilde{T})$ a non monotonic dependence from $\tilde{T}$ with a minimum.

The fundamental point is that, in these cases, the σ isn't function of the temperature alone but also of concentrations. Therefore, if one wants to study these cases, he must postulate a surface phase model with more degrees of freedom, adding, among the state parameters the concentrations of the species. The problem is more complex because it is necessary to consider also the case of absence of chemical equilibrium between the interface and the volume phases.

6. SURFACE BALANCE EQUATIONS

Surface balance equations have been derived, for particular cases, by Prud'homme (1971), Bedaux et al. (1976) and Napolitano (1977b, 1978a). The derivation presented here clarifies a number of important points and validates and/or generalizes the results obtained in the above mentioned works.
Let S(t) be an arbitrary surface bounded by the closed curve C(t). Consider as control colume Vc(t) the volume generated, at each instant t, by the parallel displacement of the bounded surface S(t) by amounts ($\pm\varepsilon$). Vc is delimited by the surface $A^\pm$ distant ($\pm\varepsilon$) from S and by the lateral surface A_ℓ passing through C(t) and normal to the parallel surface S, $A^\pm$. The outward unit normal $\hat{\underline{n}}_\ell$ to A_ℓ is a function of both $\underline{\ell}^*$ and n and can be expressed in terms of the unit normal $\underline{n}_\ell$ on C and of the components of the curvature tensor $\underline{\underline{K}}$ (Napolitano 1978b).
For a scalar extensive property X, if x , $\underline{\varphi}_n$, $\dot{x}$ denote its volume-density, total flux and production, the balance equation relative to the control volume Vc, reads:

$$\frac{d}{dt}\int_{S(t)}\left[\int_{-\varepsilon}^{\varepsilon} x\,H(n)\,dn\right]dS + \oint_{C(t)}\left[\int_{-\varepsilon}^{\varepsilon} \hat{\underline{n}}_\ell\cdot(\underline{\varphi}_n - \underline{w}\,x)\,f(n)\,dn\right]dC + \int_{A^+\cup A^-} \underline{n}\cdot(\underline{\varphi}_n - \hat{\underline{w}}\,x)\,dA = \int_{S(t)}\left[\int_{-\varepsilon}^{+\varepsilon} \dot{x}\,H(n)\,dn\right]dS \qquad (6.1)$$

where $H(n)=1+nK+n^2K_T$; $f(n)=|\underline{\lambda}+n\underline{\lambda}\cdot\underline{\underline{K}}|$

and $\underline{\lambda}$ unit vector tangent to C

$\hat{W}$ is the velocity field of the surface bounding Vc. This equation can be used to derive a number of different approximations to the balance equations for thin films. If Kmax is the largest value of the principal curvature of S, for ε Kmax<<1 it is :

H(n)≐1; f(n)≐1 and, similarly, $\hat{\underline{n}}_\ell \simeq \underline{n}_\ell$. Hence by taking the limit of eqn 6.1 for $\varepsilon \to 0$, letting:

$$\tilde{\chi} = \lim_{\varepsilon \to 0} \int_{-\varepsilon}^{+\varepsilon} \chi \, dn \; ; \; \tilde{\varphi}_\chi = \int_{-\varepsilon}^{+\varepsilon} \varphi_\chi \, dn \quad ; \quad \dot{\chi} = \lim_{\varepsilon \to 0} \int_{-\varepsilon}^{+\varepsilon} \dot{\chi} \, dn \quad (6.2)$$

and denoting by

$$\delta f = f^+ - f^- = f(\eta^*, n = 0^+, t) - f(\eta^*, n = 0^-, t)$$

he jump of a property f across S one gets:

$$\frac{d}{dt}\int_{S(t)} \tilde{\chi} \, dS + \oint_{C(t)} \underline{n}_\ell \cdot \left(\tilde{\varphi}_\chi - \underline{w}\tilde{\chi}\right) dC + \int_{S(t)} \left\{ \delta\left[\underline{n} \cdot \left(\varphi_\chi - \underline{w}\,\chi\right)\right] - \dot{\hat{\chi}} \right\} dS = 0 \quad (6.3)$$

This is the integral form of the balance equation of a scalar extensive property X for an arbitrary surface S(t) bounded by the closed curve C(t), when it is possible to define, on S, a surface density ($\tilde{\chi}$), a production $\dot{\hat{\chi}}$ per unit area and time and a flux ($\tilde{\varphi}_\chi$) per unit length. If the normal flux of X across S and x are continuous, the jump term disappears. If the surface S(t) is closed the line integral over C disappears, and, as before, the equation holds for ($\varepsilon K_{max} \ll 1$).

The local form of the balance equation is obtained by transforming the first two terms of eqn 6.3 into integrals over S(t) :

$$\frac{d}{dt}\int_{S(t)} \tilde{\chi} \, dS = \int_{S(t)} \left[\left(\frac{\partial \tilde{\chi}}{\partial t}\right)_\eta + \tilde{\chi} \, \underline{\nabla}_s \cdot \underline{w} \right] dS = \int_{S(t)} \left[\frac{\partial \tilde{\chi}}{\partial t} + \underline{\nabla}_s \cdot \left(\underline{w}\,\tilde{\chi}\right) \right] dS$$

$$\oint_{C(t)} \underline{n}_\ell \cdot \left(\tilde{\varphi}_\chi - w\,\tilde{\chi}\right) dC = \int_{S(t)} \underline{\nabla}_s \cdot \left[\tilde{\varphi}_\chi - \underline{n}\left(\underline{n} \cdot \tilde{\varphi}_\chi\right) - \underline{w}_n \tilde{\chi} \right] dS$$

Substitute these eqns into eqn 6.3, and set the resulting integral equal to zero (upon the arbitrariness of S(t) and the assumed absence of line discontinuities on it) to get:

$$\frac{\partial \tilde{\chi}}{\partial t} + \underline{\nabla}_s \cdot \left[\tilde{\varphi}_\chi - \underline{n}\left(\underline{n} \cdot \tilde{\varphi}_\chi\right) + \underline{n}\, w_n \tilde{\chi} \right] + \delta\left[\underline{n} \cdot \left(\varphi_\chi - \underline{w}\,\chi\right)\right] = \dot{\tilde{\chi}} \quad (6.4)$$

As written, eqns (   ) and (   ) apply to both scalar and vectorial properties. In the latter case surface and volume fluxes are second order tensors.

From the above equations the following useful relations are readily deduced:

$$\lim_{\varepsilon \to 0} \int_{V_d(t)} \frac{\partial \chi}{\partial t} \, dV = \int_{S(t)} \left[\frac{\partial \tilde{\chi}}{\partial t} + w_n \left(K \tilde{\chi} - \delta \chi\right) \right] dS$$

$$\lim_{\varepsilon \to 0} \int_{V(t)} \underline{\nabla} \cdot \underline{F} \, dV = \int_{S(t)} \left\{ \underline{\nabla}_s \cdot \left[\tilde{\underline{F}} - \underline{n}\left(\underline{n} \cdot \tilde{\underline{F}}\right) \right] + \delta\left(\underline{n} \cdot \underline{F}\right) \right\} dS$$

The diffusive flux $\underline{J}_\chi$ of X in the volume phases is defined by:

$$\varphi_\chi = \underline{V}\chi + \underline{J}_\chi \qquad (6.5)$$

where $\underline{V}$ is the corresponding mass velocity. An analogous separation between convective and diffucive fluxes is made for the surface total flux:

$$\tilde{\varphi}_\chi = \underline{v}\,\tilde{\chi} + \tilde{\underline{J}}_\chi \qquad (6.6)$$

The actual definition of the convective flux ($\underline{v}\,\tilde{\chi}$) must be done consistently within the framework of the whole theory. Indeed from the thermodynamic point of view the partition 6.6 implies, for instance, that the diffusive flux of a scalar property is the only part of the total flux contributing to the surface production of entropy. Hence, in principle, one should leave $\underline{v}$ undefined, proceed to the derivation of the expression for s, impose the conditions ensuring that it be always non negative and check whether, and to what extent, these requirements determine v. However, it seems appropriate to assume that the surface dissipative fluxes are the limits for of the corresponding dissipative fluxes in the volume phases. The validity of this assumption, as that of the entire theory based on the shifting equilibrium hypothesis (Napolitano 1971) underlying the local formulation of equilibrium thermodynamics, can only be verified, a posteriori, on the basis of the results it leads to, as known and as stressed by Bedaux et al. (1976). From eqns 6.4 and 6.6, formally:

$$\tilde{\varphi}_x - \underline{n}(\underline{n}\cdot\tilde{\varphi}_x) = \underline{v}_s\tilde{x} + \tilde{\underline{J}}_x - \underline{n}(\underline{n}\cdot\tilde{\underline{J}}_x) = \underline{v}_s\tilde{x} + \underline{j}_x \qquad (6.7)$$

and thus the above mentioned assumption amounts to define $\underline{j}_x$ as:

$$\underline{j}_x = \lim_{\varepsilon\to 0}\int_{-\varepsilon}^{+\varepsilon} \underline{J}_x - \underline{n}(\underline{n}\cdot\underline{J}_x)\,dn \qquad (6.8)$$

Substituting this definition of $\underline{j}_x$ into eqn 6.7 and accounting for eqns 6.2 and 6.3 yields:

$$\underline{v}_s = \frac{1}{\tilde{x}}\lim_{\varepsilon\to 0}\int_{-\varepsilon}^{+\varepsilon} x\,\underline{V}_s\,dn = \frac{1}{\tilde{\rho}}\lim_{\varepsilon\to 0}\int_{-\varepsilon}^{+\varepsilon} \rho\,\underline{V}_s\,dn \qquad (6.9)$$

where the second equality follows from the definition .
Hence the assumption 6.8 suffices to define only the tangential component $\underline{v}_s$, of $\underline{v}$. According to eqn 6.9, $\underline{v}_s$ is the tangential mass velocity of the surface phase. The component vn will be left for the moment unspecified. It will be later shown that the above mentioned requirements for S lead to the definition $v_n = w_n$

For scalar properties the balance equations involve only tangential fluxes. Hence there is no need to impose the vanishing of normal diffusive surface fluxes because j_x is "automatically" a surface vertor. For vectorial properties with symmetric diffusive fluxes in the volume phases assumption 6.8 implies that $\underline{j}_x$ is a surface tensor ($\underline{n}\cdot\underline{j}_x = \underline{j}_x\cdot\underline{n} = \underline{0}$). For a non-symmetric diffusive tensorial flux $\underline{J}_x$ the left normal vectorial component $\underline{n}\cdot j_x$ (normal flux of the tangential component of X) still vanishes automatically. The right normal component $\underline{j}_x\cdot\underline{n}$ (tangential flux of the normal component of X) does not vanish and, consequently, $\underline{j}x$ is not a surface tensor.

With the definition 6.5 and 6.7 eqn 6.4 becomes:

$$\frac{\partial\tilde{x}}{\partial t} + \underline{\nabla}_s\cdot\left[\underline{v}_s\tilde{x} + \underline{j}_x\right] + \delta\left[z_n x + \underline{n}\cdot\underline{J}_x\right] = \dot{\tilde{x}} - w_n\tilde{x}K \qquad (6.10)$$

$$\left[z_n = \underline{n}\cdot(\underline{V} - \underline{w})\right]$$

where the last terms in the r.h.s. follows from the vectorial identity $\underline{\nabla}_s\cdot(w_n\tilde{x}\underline{n}) = w_n\tilde{x}K$.
This equation describes the balance of X in the area element dA of the surface S. The local time rate of change is due to the interaction between tha area element and its environment and to the production of X on dA. The environment of dA is constituted by adjacent surface and volume elements. Interaction with contiguous surface elemens takes place through the surface curve bounding dA and is described by the surface divergence term. Interaction with the adjacent volume elements takes place through the positive and negative faces of dA and is described by the jump term. The first term on the r.h.s. of eqn 6.10 describes the "physical" production and vanishes for conservative properties. The second one is also to be interpreted as a production term. It is related to the rate of area change per unit area ($w_n K$) due to local warping of the surface "geometrical" production. The component $\underline{w}_s$ does not appear explicitly in eqn

6.10. This implies that the question of whether or not $\underline{w}_s = \underline{v}_s$ (material surface assumption) is irrelevant for the local form of the balance equation so that the more general validity of the equation derived by Prud'homme (1971) under this assumption is proved.

6.1 Continuity equation. Alternate forms of balance equations

For X = M , the total mass, $\underline{J}_x$ and $\underline{j}_x$ vanish identically upon the definition of $\underline{V}$ and $\underline{v}_s$; $\dot{\hat{x}} = 0$ upon the principle of mass conservation, and eqn 6.10 yields the surface continuity equation:

$$\frac{\partial \tilde{\rho}}{\partial t} + \underline{\nabla}_s \cdot \underline{v}_s \tilde{\rho} + \delta\left[z_n \rho\right] = - w_n \tilde{\rho} K \qquad (6.11)$$

A surface substantial derivative is defined as:

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \underline{v}_s \cdot \underline{\nabla}_s \qquad (6.12)$$

From eqns 6.10, 6.11, 6.12:

$$\frac{d\tilde{\rho}}{dt} + \tilde{\rho}\, \underline{\nabla}_s \cdot \underline{v}_s + \delta\left[z_n \rho\right] = - w_n \tilde{\rho} K$$

$$\frac{d\hat{x}}{dt} + \hat{x}\, \underline{\nabla}_s \cdot \underline{v}_s + \underline{\nabla}_s \cdot \underline{j}_x + \delta\left[z_n (x - \rho \hat{x}) + \underline{n} \cdot \underline{J}_x\right] = \dot{\hat{x}}$$

$$(6.13)$$

from which the surface balance equation in terms of specific quantities $\bar{x}$ ($\tilde{\rho}\bar{x} = \hat{x} \Rightarrow \tilde{\rho}\, d\bar{x} = d\hat{x} - \bar{x}\, d\tilde{\rho}$) follows

$$\tilde{\rho} \frac{d\bar{x}}{dt} + \underline{\nabla}_s \cdot \underline{j}_x + \delta\left[z_n\left(x - \rho \bar{x}\right) + \underline{n} \cdot \underline{J}_x\right] = \dot{\hat{x}} \qquad (6.14)$$

Notice that only the "physical" production appears in this form of the balance equation.
The continuity equation can be formulated also in terms of the area per unit mass $\bar{\omega}$. From eqn 6.12 one gets ($\tilde{\rho}\bar{\omega} = 1 \Rightarrow \tilde{\rho}\, d\bar{\omega} = -\bar{\omega}\, d\tilde{\rho}$):

$$\tilde{\rho} \frac{d\bar{\omega}}{dt} - \delta\left[z_n \rho \bar{\omega}\right] = \underline{\nabla}_s \cdot \underline{v}_s + w_n K \qquad (6.15)$$

As expectable, the diffusive flux of area vanishes. The terms ($\underline{\nabla}_s \cdot \underline{v}_s$) and $w_n K$ can be interpreted as the "physical" and "geometrical" production of surface area.

6.2 Momentum equation

From the general expression 6.14 one gets, for the momentum equation:

$$\tilde{\rho} \frac{d\underline{v}}{dt} - \underline{\nabla}_s \cdot \underline{\underline{\Pi}} + \delta\left[z_n \rho\left(\underline{V} - \underline{v}\right) - \underline{n} \cdot \underline{\underline{\Gamma}}\right] = \tilde{\rho}\, \underline{g} \qquad (6.16)$$

where $\underline{\underline{\Pi}}$ and $\underline{\underline{\Gamma}}$ are the surface and volume stress tensors, and $\underline{g}$ is the gravitational vector. It is assumed that both volume phases are non-micro polar, non elastic fluids. In this case, $\underline{\underline{T}}$ is symmetric, $\underline{\underline{\Pi}}$ consequently is a two-dimensional surface tensor, and:

$$\underline{\underline{\Gamma}} = - p\, \underline{\underline{M}} + \underline{\underline{T}} \quad ; \quad \underline{\underline{\Pi}} = \sigma\, \underline{\underline{M}}_s + \underline{\underline{\Sigma}} \qquad (6.17)$$

where p is the thermodynamic pressure (or mean non-dissipative normal stress). $\underline{\underline{U}}$ and $\underline{\underline{U}}_s$ are the volume and surface unit tensors, $\underline{\underline{T}}$ is the viscous stress tensor and, as it will appear later, $\underline{\underline{\Sigma}}$ is the dissipative part of $\underline{\underline{\Pi}}$.

The surface total derivative of the unit normal $\underline{n}$ is, upon eqns 6.12:

$$\frac{d\underline{n}}{dt} = \underline{v}_s \cdot \underline{\underline{K}} - \underline{\nabla}_s w_n$$

With the help of this equation one obtains the expression for the normal and tangential components of the acceleration $\underline{a}$:

$$a_n = \frac{dv_n}{dt} - \underline{v}_s \cdot \frac{d\underline{n}}{dt} = \frac{dv_n}{dt} + \underline{v}_s \cdot \underline{\nabla}_s w_n - \underline{v}_s \cdot \underline{\underline{K}} \cdot \underline{v}_s$$

$$\underline{a}_s = \underline{n} \wedge (\underline{a} \wedge \underline{n}) = \underline{v}_s \cdot \underline{\underline{K}}\, v_n - v_n \underline{\nabla}_s w_n + \underline{n} \wedge \left(\frac{d\underline{v}_s}{dt} \wedge \underline{n}\right)$$

The corresponding normal and tangential projections of the momentum equations 6.16 read, on account of eqns 6.17:

$$\tilde{\rho}\, a_n + \sigma K + \underline{\underline{\Sigma}} : \underline{\underline{K}} + \delta\left[z_n \rho (V_n - v_n) + p - \underline{n} \cdot \underline{\underline{T}} \cdot \underline{n}\right] = \tilde{\rho}\, g_n$$
$$\tilde{\rho}\, \underline{a}_s - \underline{\nabla}_s \sigma - (\underline{\nabla}_s \cdot \underline{\underline{\Sigma}})_s + \delta\left[z_n \rho (\underline{V}_s - \underline{v}_s) - (\underline{n} \cdot \underline{\underline{T}})_s\right] = \tilde{\rho}\, \underline{g}_s \qquad (6.18)$$

The first equation generalizes, to the present case, the Laplace formula $\sigma K + \delta p = 0$.

As for volume phases, the surface particle acceleration can also be expressed in terms of the curl of $\underline{v}$ through eqn 6.12:

$$\underline{a} = \frac{\partial \underline{v}}{\partial t} + \underline{\nabla}_s \frac{v^2}{2} + (\underline{\nabla}_s \wedge \underline{v}) \wedge \underline{v}$$

from which, upon using Gibbs equation in terms of the surface enthalpy, the following equivalent expression of the momentum equation is obtained:

$$\frac{\partial \underline{v}}{\partial t} + \underline{\nabla}_s \bar{H}_s + (\underline{\nabla}_s \wedge \underline{v}) \wedge \underline{v} = \tilde{T}\, \underline{\nabla}_s \bar{s} + \tilde{y}_i\, \underline{\nabla}_s \bar{\mu}_i +$$

$$+ \bar{\omega}\left\{\left[(\underline{\nabla}_s \cdot \underline{\underline{\Sigma}})_s - \underline{\underline{\Pi}} : \underline{\underline{K}}\, \underline{n}\right] + \delta\left[z_n \rho (\underline{v} - \underline{V}) - \underline{n} p + \underline{n} \cdot \underline{\underline{T}}\right]\right\} \qquad (6.19)$$

where:

$$\bar{H}_s = \bar{h} + \frac{v^2}{2} + \psi \qquad \underline{g} = -\underline{\nabla} \psi$$

can be referred to as the specific surface total enthalpy. Equation 6.19 together with the energy conservation equation, to be derived in the next paragraph, constitue the starting point for the study of fluid-dynamic properties of the surface phase analogous to those expressed, for volume phases, by Bernoulli's and Crocco theorems.

6.3 Energy equation

The specific total surface energy e is given by:

$$\bar{e} = \bar{u} + \frac{v^2}{2} + \psi$$

where ψ is the potential energy. Balance equations for ψ and $\bar{u}$ are formulated according to the definition of ψ ($\underline{g} = -\underline{\nabla}\psi$) and to the general expression 6.14 and read, on account of eqn 6.12:

$$\tilde{\rho}\, \frac{d\psi}{dt} = -\tilde{\rho}\, \underline{g} \cdot \underline{v} \qquad \tilde{\rho}\, \frac{d\bar{u}}{dt} + \underline{\nabla}_s \cdot \underline{j}_u + \delta\left[z_n (u - \rho \bar{u}) + \underline{n} \cdot \underline{J}_u\right] = \dot{\hat{u}} \qquad (6.20)$$

where, in the first equation, account has been taken of the fact that, contrary to $\bar{u}$ and $\underline{v}$, ψ is also function of n.

The balance equation for the kinetic energy is obtained from the momentum equation 6.16 upon scalar multiplication by $\underline{v}$ and reads:

$$\tilde{\rho}\frac{d}{dt}\left(\frac{v^2}{2}\right) - \underline{\nabla}_s\cdot\left(\underline{\underline{\Pi}}\cdot\underline{v}_s\right) + \underline{\underline{\Pi}} : \underline{\nabla}_s\underline{v} + \delta\left[z_m\rho\left(\underline{V}-\underline{v}\right)\cdot\underline{v} - \underline{n}\cdot\underline{\underline{\Gamma}}\cdot\underline{v}\right] = \tilde{\rho}\underline{g}\cdot\underline{v} \qquad (6.21)$$

The surface total energy conservation equation reads, upon eqn 6.16:

$$\tilde{\rho}\frac{d\bar{e}}{dt} + \underline{\nabla}_s\cdot\underline{j}_e + \delta\left[z_m\left(e-\rho\bar{e}\right) + \underline{n}\cdot\underline{J}_e\right] = 0 \qquad (6.22)$$

where the diffusion flux $\underline{J}_e$ and the total energy density e in the volume phase are given by (De Groot and Mazur, 1962):

$$\underline{J}_e = \underline{J}_u - \underline{\underline{\Gamma}}\cdot\underline{V} \quad ; \quad e = u + \rho\left(\frac{V^2}{2} + \Psi\right) \qquad (6.23)$$

Adding eqns 6.20, 6.21, accounting for eqns 6.23 and comparing the result with eqn 6.22 lead to

$$\underline{j}_e = \underline{j}_u - \underline{\underline{\Pi}}\cdot\underline{v}_s \qquad (6.24)$$

$$\dot{\tilde{u}} = \underline{\underline{\Pi}} : \underline{\nabla}_s\underline{v} - \delta\left[z_m\rho\frac{\left(\underline{V}-\underline{v}\right)\cdot\left(\underline{V}-\underline{v}\right)}{2} - \underline{n}\cdot\underline{\underline{\Gamma}}\cdot\left(\underline{V}-\underline{v}\right)\right] \qquad (6.25)$$

The first equation is the surface equivalent of eqn 6.23. The internal energy production contains, in addition to the power density associated with the deformation of the surface particle, jump terms from velocity differences between surface and volume phases.

The energy conservation equation can be formulated in terms of the total specific enthalpy $\bar{H}_s$ and, on account of eqns 6.15, 6.17, and 6.22 through 6.24 reads:

$$\tilde{\rho}\frac{d\bar{H}_s}{dt} + \underline{\nabla}_s\cdot\left[\underline{j}_u - \underline{\underline{\Sigma}}\cdot\underline{v}_s + \sigma w_n K + \frac{\partial\sigma}{\partial t}\right] + \delta\left[z_m\left(H-\rho\bar{H}_s\right) + \underline{n}\cdot\underline{J}_u + w_n p - \underline{n}\cdot\underline{\underline{T}}\cdot\underline{V}\right] = 0 \qquad (6.26)$$

where $H = h + \rho\left[\frac{V^2}{2} + \Psi\right]$ is the total enthalpy density in the volume phases.

6.4 Surface entropy production

The surface entropy balance equation reads, upon eqn 6.14:

$$\tilde{\rho}\frac{d\bar{s}}{dt} + \underline{\nabla}_s\cdot\underline{j}_s + \delta\left[z_m\left(s-\rho\bar{s}\right) + \underline{n}\cdot\underline{J}_s\right] = \dot{\tilde{s}} \qquad (6.27)$$

The entropy density (s) and diffusive flux ($\underline{J}_s$) in the volume phase satisfy the Euler and diffusive flux relations (De Groot and Mazur, 1962):

$$u = Ts - p + y_i x_i \quad ; \quad \underline{J}_u = T\underline{J}_s + y_i\cdot\underline{J}_i \qquad (6.28)$$

A summation with respect to the index (i) is implied in eqns 6.14 The range of values for (i) is taken to be the same for the surface and the two volume phases with x_i (resp. x_i) and y_i (resp. y_i) formally equal to zero for the property which does not enter the thermodynamic description of the volume (resp. surface) phase. From the surface Gibbs equation ( ) one gets:

$$\tilde{\rho}\frac{d\bar{u}}{dt} = \tilde{\rho}\left[\hat{T}\frac{d\bar{s}}{dt} + \sigma\frac{d\bar{\omega}}{dt} + \hat{y}_i\frac{d\bar{x}_i}{dt}\right] \qquad (6.29)$$

Substitute into this equation the surface substantial derivatives obtained from the balance eqns (6.4), (6.15), (6.20)$_2$ and (6.21), account for the (6.19)$_2$

$$\underline{j}_s = \tilde{T}\,\underline{j}_s + \tilde{y}_i\,\underline{j}_i \qquad (6.30)$$

$$\begin{aligned}\tilde{T}\dot{s} = {} & \underline{\underline{\Pi}} : \nabla_s \underline{v} - \sigma\left(\nabla_s\cdot\underline{v}_s + w_n K\right) - \tilde{y}_i\,\dot{x}_i - \underline{j}_s\cdot\nabla_s\tilde{T} - \underline{j}_i\cdot\nabla_s\tilde{y}_i \\ & + \delta\Big\{Z_n\Big[p + \left(\tilde{T} - T\right)s + \left(\tilde{y}_i - y_i\right)x_i - \rho\,\frac{(\underline{V}-\underline{v})\cdot(\underline{V}-\underline{v})}{2} \\ & + \underline{n}\cdot\Big[\left(\tilde{T} - T\right)\underline{J}_s + \left(\tilde{y}_i - y_i\right)\underline{J}_i - \underline{\underline{\Gamma}}\cdot(\underline{v}-\underline{V})\Big]\Big]\Big\}\end{aligned} \qquad (6.31)$$

Equation (6.30) is the surface equivalent of eqn (6.19) and could have been written a priori since it follows necessarily from the Euler expression (4.3) (Napolitano 1971) on account of the vanishing of the area diffusive flux.

The expression for the entropy production must be further transformed to bring forth the independent generalized forces. Decompose $\underline{\underline{\Gamma}}$ as (Napolitano 1977):

$$\underline{\underline{\Gamma}} = -p\,\underline{\underline{U}} + \underline{n}\,t_n\,\underline{n} + \underline{n}\,\underline{t} + \underline{t}\,\underline{n} + \underline{\underline{T}}_s$$

with $\underline{t}$ and $\underline{\underline{T}}_s$ surface vector and tensor, respectively, and account for eqn (6.17) to get:

$$\begin{aligned}\underline{\underline{\Pi}} : \nabla_s\underline{v} - \sigma\left(\nabla_s\cdot\underline{v}_s + w_n K\right) - \delta\left[\underline{n}\cdot\underline{\underline{\Gamma}}\cdot(\underline{v}-\underline{V})\right] = {} & \underline{\underline{\Sigma}} : \nabla_s\underline{v} \, + \\ + \left(V_n - W_n\right)\left[\sigma K + \delta\left(p - t_n\right)\right] - \delta\Big[Z_n\left(p - t_n\right) & + \underline{t}\cdot\left(\underline{v}_s - \underline{V}_s\right)\Big)\end{aligned} \qquad (6.32)$$

Positivity of the surface entropy production cannot be imposed if the number of generalized forces exceeds that of generalized fluxes. From eqns (6.3) and (6.32) it follows then that, necessarily, $v_n = W_n$. No further restriction arises from the equations and, therefore, the assumed definition of v_s appears to be innerly consistent.

6.5 Phenomenological relations

From the expression for $\dot{s}$ obtained by combining eqns ((6.31)and (6.32)) one deduces the following set of generalized force-flux couples:

$$\begin{aligned}&\left\{\underline{\underline{\Sigma}}_0,\,(\nabla_s\underline{v})_0^s/\tilde{T}\right\};\ \Big\{\left[\underline{j}_s,\,-\nabla_s\tilde{T}/\tilde{T}\right];\left[\underline{j}_i,\,-\nabla_s\tilde{y}_i/\tilde{T}\right] \\ &\left[-\underline{t}^t,\,\pm(\underline{v}_s-\underline{V}_s^t)/\tilde{T}\right]\Big\};\Big\{\left[(\sigma_m-\sigma),\,\nabla_s\cdot\underline{v}/\tilde{T}\right];\ \left[-\dot{\xi}_j,\,A_j/\tilde{T}\right] \\ &\left[t_n^t + B,\,(V_n^t - v_n)/\tilde{T}\right];\left[J_s^t,\,\pm(\tilde{T}-T^t)/\tilde{T}\right];\left[J_i^t,\,(\tilde{y}_i-y_i^t)/\tilde{T}\right]\Big\}\end{aligned} \qquad (6.33)$$

where $(\;\;)^t$ denotes volume phases values for $n = 0^t$, respectively, $\underline{\underline{\Sigma}} = (\sigma_m - \sigma)\,\underline{\underline{U}}_s + \underline{\underline{\Sigma}}_0$ with σ_m the mean surface normal stress and $\underline{\underline{\Sigma}}_0$ the traceless part of $\underline{\underline{\Sigma}}$; $(\nabla_s\underline{v})_0^s$ denotes the traceless symmetric part of $(\nabla_s\underline{v})$, B is equal to the coefficient of Z_n in eqn (6.30), less the (p), $J_s = \underline{n}\cdot\underline{J}_s$; $J_i = \underline{n}\cdot\underline{J}_i$; $\dot{\xi}_j$ denotes the set of independent progress variables for the surface productions $\dot{x}_i$ and the Aj are the corresponding affinities.

Linear phenomenological laws are established in the standard manner upon accounting for the tensorial order of the above three set of force-flux couples, the isotropy of the surface and volume phases and Curie's principle (De Groot and Mazur, 1962; Bedaux et al., 1976). The first set leads to (Bedaux et al., 1976; Napolitano, 1977):

$$\underline{\underline{\Sigma}}_s = 2\eta_s (\underline{\nabla}_s \underline{v})_s^s \qquad \eta_s > 0$$

where η_s is the surface shear viscosity coefficient and the inequality follows from the positivity of entropy production.
For the second set, let (k) be the number of couples, and $\underline{F}$, $\underline{f}$ denote the k-dimensional column matrices of generalized fluxes and forces. Then the linear phenomenological relations are formally expressed by:

$$\underline{F} = \underline{\underline{L}} \cdot \underline{f}$$

with $\underline{\underline{L}}$ the k-dimensional matrix of kinetic coefficients. The independent set of forces, provided the fluxes are also suitable transformed, can be transformed into another independent set. If $\underline{f}' = \underline{\underline{A}} \cdot \underline{f}$ is the column matrix of the new set of forces, with $\underline{\underline{A}}$ a regular matrix, the new set of fluxes $\underline{F}$ is given by $\underline{F}' = (\underline{\underline{A}}^{-1})^T \cdot \underline{F}$ (where the superscript (T) denotes transportation) and the new matrix of kinetic coefficient is given by $\underline{\underline{L}}' = (\underline{\underline{A}}^{-1})^T \cdot \underline{\underline{L}} \cdot \underline{\underline{A}}^{-1}$. With the help of these transformation formulae the entropy diffusive flux may be eliminated on favor of the diffusive flux of internal energy (by means of eqn (6.30)) and the new set of generalized forces can be readily found. As with volume phases, there is no unique definition of surface heat flux $\underline{J}_q$ if the $\underline{J}_i$ are different from zero. Common choices are $\underline{J}_q = \underline{J}_e$ and $\underline{J}_q = T\underline{J}_s$ but others may be given.

Besides the usual cross- coupling effects between the surface diffusion of entropy and scalar extensive properties $\tilde{X}_i$ there is a coupling between these surface diffusions and the exchange of tangential momentum between the surface and the volume phases.

Onsager relations among the cross-coupling coefficients are readily established when account is taken of the behaviour of generalized forces under time reversal (De Groot and Mazur, 1962; Bedaux et al., 1976). Likewise, inequalities following from the positivity of the entropy production are readily formulated.

An analogous development can be made for the phenomenological relations among the third set of scalar force-flux couples in (6.33). Thus, for instance, the surface dissipative diffusion of normal momentum ($\sigma_m - \sigma$) is coupled with the exchanges of normal momentum, entropy and properties between surface and volume phases as well as with the surface productions.

As seen, phenomenological relations for he surface phase need to be formulated also for the normal fluxes t_n^s, $\underline{t}^s$, $\underline{J}_s^s$, $\underline{J}_i^s$ which are described, in the volume phases, by other phenomenological relations (much simpler, in general, because of the smaller number of coupling effects). The values yielded by these couples of phenomenological relations on each of the faces of the surface must be equal. This obvious requirement yields additional interface boundary conditions for the volume phase field equations (Bedaux et al., 1976).

7. FIELD EQUATIONS AND THEIR NON-DIMENTIONAL FORM

7.1 Volume Phases

It is assumed that volume phases are constitued by non-elastic, non-micropolar Newtonian fluids with negligible bulk viscosity, that the motion is steady, that the Boussinesqu and constant transport properties approximations apply and that radiation effects are negligible.

With these hypotesis, the closed set of field equations for the volume phases reads:

$$\rho = \rho_0\left(1 - \beta_T\left(T - T_0\right)\right) \qquad \underline{\nabla}\cdot\underline{V} = 0$$

$$\underline{V}\cdot\underline{\nabla}\underline{V} + \frac{1}{\rho_0}\underline{\nabla}p = \frac{\rho}{\rho_0}\underline{g} + \nu\nabla^2\underline{V} \qquad (7.1)$$

$$\underline{V}\cdot\underline{\nabla}T = \alpha\nabla^2 T + \frac{\nu}{c_v}\phi$$

where:

$$\alpha = \lambda/\rho_0 c_v \qquad \beta_T = -\left(\partial \ln\rho/\partial T\right)_p = \text{const}$$

$$\nu = \mu/\rho_0 \qquad \phi = 2\left(\underline{\nabla}\underline{V}\right)^s : \left(\underline{\nabla}\underline{V}\right)^s$$

μ and λ are the coefficient of viscosity and heat conduction, the subscript (o) denotes values in a reference state and all other symbol have their usual meanings.

For gas phases the energy equation involves the further approximation that potential energy is negligible with respect to internal energy.

The formulation of surface-phase field equations and a correct order of magnitude analysis of surface-driven flows require the use of a coordinate system in which components tangent and normal to the interface S of vectors, tensors and differential operators appears separately in the field equation.

The coordinates (ξ^1, ξ^2, ζ) of such a system, referred to a parallel surface coordinate system, are arbitrary curvilinear coordinates (ξ^1, ξ^2) on the surface S and the Euclidean distance ζ from S. Properties of this system were developed in chapter. (2)

In the parallel surface coordinate system equation (7.1) read:

Continuity:

$$\underline{\nabla}_t\cdot\underline{V}_t + \frac{\partial V_n}{\partial\zeta} + V_n C = 0 \qquad (7.2)$$

Normal Momentum:

$$V_n\frac{\partial V_n}{\partial\zeta} + \underline{V}_t\cdot\underline{\nabla}_t V_n - \underline{V}_t\cdot\underline{\underline{C}}\cdot\underline{V}_t + \frac{1}{\rho_0}\frac{\partial p}{\partial\zeta} =$$

$$= \frac{\rho}{\rho_0}g_n - \nu\,\underline{\nabla}_t\cdot\underline{\bar{\Omega}}_t \qquad (7.3)$$

Tangential Momentum:

$$V_n \frac{\partial \underline{V}_t}{\partial \zeta} + \underline{V}_t \cdot \left(\underline{\nabla}_t \underline{V}_t\right)_t + V_n \underline{V}_t \cdot \underline{\underline{C}} + \frac{1}{\rho_0} \underline{\nabla}_t p = \frac{\rho}{\rho_0} \underline{g}_t + \nu \left\{ \frac{\partial \underline{\bar{\Omega}}_t}{\partial \zeta} - \underline{\bar{\Omega}}_t \cdot \left(\underline{n} \wedge \underline{\underline{C}} \wedge \underline{n}\right) + \underline{n} \wedge \underline{\nabla}_t \Omega_n \right\} \qquad (7.4)$$

Internal Energy:

$$V_n \frac{\partial T}{\partial \zeta} + \underline{V} \cdot \underline{\nabla}_t T = \alpha \left[\underline{\nabla}_t \cdot \underline{\nabla}_t T + \frac{\partial T}{\partial \zeta} C + \frac{\partial^2 T}{\partial \zeta^2} \right] + \frac{2\nu}{c_v} \left\{ \left(\frac{\partial V_n}{\partial \zeta} \right)^2 + \frac{1}{2} \underline{\bar{\Omega}}_t \cdot \underline{\bar{\Omega}}_t + \left[V_n \underline{\underline{C}} + \left(\underline{\nabla}_t \underline{V}_t\right)_t^s \right] : \left[V_n C + \left(\underline{\nabla}_t \underline{V}_t\right)_t^s \right] \right. \qquad (7.5)$$

where:

$$\underline{\bar{\Omega}}_t = \frac{\partial \underline{V}_t}{\partial \zeta} - \underline{\nabla}_t V_n + \underline{\underline{C}} \cdot \underline{V}_t = \underline{\Omega} \wedge \underline{n} \qquad \Omega_n = \underline{\nabla}_t \cdot \left(\underline{V}_t \wedge \underline{n}\right)$$

$\underline{\underline{C}} = \underline{\nabla}_t \underline{n}$ is the symmetric curvature tensor of coordinate surface $\zeta =$ const. C its trace and $\underline{\Omega}_t$, Ω_n are the components of $\underline{\Omega} = \underline{\nabla} \wedge \underline{V}$

7.2Surface phase

The surface phase is assumed to be a thermodynamic system with only one intensive degree of freedom in thermal and dynamic equilibrium with the two volume phases.

The surface tension will be taken to vary linearly with the absolute temperature and surface irreversibility will be neglected.

The above thermodinamic model implies that the surface has no bending or warping elasticity (the equilibrium surface stress tensor is isotropic) and that:

$$\begin{aligned} \sigma &= \sigma_0 \left[1 - \frac{\sigma_T}{\sigma_0} (T - T_0) \right] \\ d\tilde{u} &= T\, d\tilde{s} \qquad\qquad (7.6) \\ \tilde{h} &= \tilde{u} - \sigma = \tilde{T}\tilde{s} = T\sigma_T \end{aligned}$$

where σ is the surface or interfacial tension, σ_0 its value in the reference state, $\bar{u}$, $\bar{s}$, and $\bar{h}$ are the surface internal energy, entropy and enthalpy per unit area, respectively, and:

$$\sigma_T = -\frac{d\sigma}{dT} = \text{constant} > 0$$

In this model surface internal energy and entropy per unit area are uniform.

With these assumptions, the surface phase fiel equations are

$$\begin{aligned} &\sigma K + \delta\left[p + 2\mu\, \underline{\nabla}_t \cdot \underline{V}_t \right] = 0 \qquad\qquad (7.7) \\ &\delta\left\{ \mu \left[\frac{\partial \underline{V}_t}{\partial \zeta} - \underline{V}_t \cdot \underline{\underline{K}} \right] \right\} = -\underline{\nabla}_t \sigma = \sigma_T \left(\underline{\nabla}_t T\right)_s \end{aligned}$$

$$\delta\left[\lambda \frac{\partial T}{\partial \zeta}\right] = T_s \sigma_T \left(\underline{\nabla}_t \cdot \underline{V}_t\right)_s = \bar{h}\left(\underline{\nabla}_t \cdot \underline{V}_t\right)_s$$

$$V_n\left(\zeta = 0^{\pm}\right) = 0 \quad ; \quad \delta \underline{V}_t = 0 \quad ; \quad \delta T = 0 \qquad (7.8)$$

where:

$$\delta f = f\left(\xi^1, \xi^2, \zeta = 0^{\pm}\right) - f\left(\xi^1, \xi^2, \zeta = 0^{-}\right)$$

denotes the jump of a properties f across S; K is the curvature tensor of S, K/2 its mean curvature and the subscript (s) denotes values for ζ = 0 (surface values).

Equation (7.7) are the surface balance equations for normal and tangential momentum and for internal energy. The first of eqs. (7.8) expresses the condition that S is a stream surface. The other two follow from the assumed thermodynamic equilibrium between surface and volume phases.

7.3 Non-dimensional Form

A non-dimensional form of the field equations is meaningfull if and only if non-dimensional coordinates and non-dimensional flow field variables as well as their derivatives are all at most of order one. To meet this requirement the definition of non dimensional quantities must involve a number of non-dimensional scale factors, as indicated below:

$$\zeta = n L_n \; ; \; \xi_i = \eta^i L_t \; (i = 1,2) ; \; L_n = \ell \ell_t L \; ; \; L_t = \ell_t L$$

$$\underline{\underline{K}} = \underline{\underline{k}} / L_c \; ; \; \underline{\underline{C}} = \underline{\underline{c}} / L_c \; ; \; L_c = \ell_c \ell_t L$$

$$\underline{\underline{k}} = \ell_c \underline{\nabla}_s^* \underline{n} \; ; \; \underline{\underline{c}} = \ell_c \underline{\nabla}_t^* \underline{u} \; ; \; \underline{V}_t = V_2 \underline{v}_t \; ; \; V_n = \ell V_2 v_n$$

$$\rho = \rho_0 \rho^* \; ; \; \sigma = \sigma_0 \sigma^* \; ; \; T = T_0 + \ell_T (\Delta T_2) \theta \qquad (7.9)$$

$$p - p_0 = p_h + p_d = p_{hc} \pi_h + \rho_2 \ell_p \pi \; ; \; \Omega_t = \frac{V_2}{\ell L_t} \omega_t \; ; \; \Omega_n = \frac{V_2}{L_t} \omega_n$$

$$\phi = \left(\frac{V_2}{\ell L_t}\right)^2 \varphi \; ; \; \underline{\nabla}_t = \frac{1}{L_t} \underline{\nabla}_t^* \; ; \; \underline{\nabla}^* = \underline{\nabla}_t^* + \frac{\underline{n}}{\ell} \frac{\partial}{\partial n}$$

Flow field length scales L_t and L_n in the directions tangential and normal to the interface may have different orders of magnitude in different regions and, in addition, are not necessarely of the same order as the geometrical length L characteristic of the problem considered. The scale factors ℓ = (L_T / L) and ℓ = L_n / L_T = $L_n / \ell_t L$ account for this fact and, consequently, are essential only when not of order one. Thus for instance, an appropriate choice of the scale factor will ensure that the non-dimensional tangential coordinates and the corresponding space derivatives of flow variables be at most of

order one in regions whose tangential extension is either much smaller (e.g. regions in the neighbourhood of confluence between solid boundaries and interfaces, $\ell_t \ll 1$) or much larger (e.g far fields, $\ell_t \gg 1$) than L. Similarly, an appropiate choice of l ensures that ζ and non-dimensional normal derivatives of flow variables be at most of order one in thin dissipative layers adjacent to the interface. Upon the continuity equation, l is also the ratio of the scales for normal and tangential velocities.
In three dimensional problems when the two length scales in directions tangential to the interface are of different order of magnitude, L_t stands for the smallest one of the two scales and their ratio will appear in the expression for $\underline{\nabla}_t^*$.

The length scale L_c normalizes the curvature tensors $\underline{\underline{K}}$ and $\underline{\underline{C}}$ and is of the same order as the smallest principal radius of curvature R_c of S since $(1/R_c)$ is the upper bound for their components. The curvature scale factor $l_c = L_c / L_t$ is at most of order one and its presence accounts for the fact that the tangential variation of the normal n in the direction corresponding to R_c may be much larger than that in the direction corresponding to L_t. Thus $l = 1$ unless $R_c / L_t << 1$ in which case $l_c = R_c / L_t << 1$. In practice, R_c can be taken equal to the smallest radius of curvature of the hydrostatic shape of S. The underlying assumption that the motion does not change the orders of magnitude of the curvatures of S appears indeed plausible as long as the motion does not cause a breacking up of the interface.

Pressures and temperatures are measured from their values (P_0, T_0) in a reference state, which depends on the problem considered. The relative pressure $(P - P_0)$ is split into "hydrostatic" pressure P_h and "dynamic" pressure P_d. Their scales (P_{hr}) and (P_r) may be of different orders of magnitude.

The role of pressure and temperature scale factors (l_p, l_T) is the same as that of the length scale factors. When there is no imposed pressure gradient l_p is irrilevant and can be taken equal to one. When P_r and T_r are determined from problem's data, l_p and l_T are to be used to analyse regions where the pressure and temperature scales are, locally, of order of magnitude different than those given by imposed pressure and temperature differences.

The reference quantities P_{hr}, (L_t), Vr and $(l_T\, \Delta T)$ are the same for both volume phases. The two latter conditions follow from eqs. (7.8) and hence are correct only when the surface-phase is in thermodynamic equilibrium with both volume phases. The scale factor l and the dynamic reference pressure (P_r) may be different in the two volume phases.
Quantities that are not expressable in terms of problem's data cannot be prescribed a-priori and must be determined from the order of magnitude analysis of the field equations.

7.3.1 Volume field equations

Substitution of eqs. (7.9) into eqns. (7.5) leads to the following non-dimensional form for the fields equations for each volume phase:

$$\rho^* = 1 - \beta \ell_T \theta$$

$$\underline{\nabla}^{+} \cdot \underline{v}_t + \frac{\partial v_n}{\partial n} + \frac{\ell}{\ell_c} v_n C = 0$$

$$\ell_t \bar{R}e\, \ell^2 \left\{ \ell^2 \left[\underline{v}_t \cdot \underline{\nabla}_t^* v_n + v_n \frac{\partial v_n}{\partial n} \right] - \frac{\ell}{\ell_c} \underline{v}_t \cdot \underline{\underline{C}} \cdot \underline{v}_t + \bar{E}_h \frac{\partial \Pi_h}{\partial n} + \ell_p \bar{E} \frac{\partial \pi}{\partial n} \right\} - \rho^* \frac{\bar{G}_r}{\beta} \ell^3 \ell_t^2\, \hat{\underline{g}} \cdot \underline{n} = \ell^2 \underline{\nabla}_t^* \cdot \left[- \frac{\partial \underline{v}_t}{\partial n} - \frac{\ell}{\ell_c} \underline{v}_t \cdot \underline{\underline{C}} + \ell^2 \underline{\nabla}_t^* v_n \right]$$

$$l_t \bar{R}_e l^2\left\{ \underline{v}_t\cdot\left(\underline{\nabla}_t^*\cdot\underline{v}_t\right)_t + v_n\frac{\partial \underline{v}_t}{\partial n} + \frac{l}{l_c} v_n \underline{v}_t\cdot\underline{\underline{C}} + \bar{E}_h \underline{\nabla}_t^* \pi_h + \right.$$

$$\left. + l_p \bar{E}\,\underline{\nabla}_t^*\pi\right\} - \rho^* \frac{G_r}{\beta} l^2 l_t^2\, \underline{\hat{g}}_t = \left\{\frac{\partial}{\partial n}\left[\frac{\partial \underline{v}_t}{\partial n} + \frac{l}{l_c}\underline{v}_t\cdot\underline{\underline{C}} - l^2\underline{\nabla}_t^* v_n\right] + \right.$$

$$\left. - \frac{l}{l_c}\bar{\underline{\omega}}_t\cdot\left(\underline{n}\wedge\underline{\underline{C}}\wedge\underline{n}\right) + l^2\underline{\nabla}_t^*\omega_n\right\} \qquad (7.10)$$

$$l_t \bar{P}_e l^2\left\{\underline{v}_t\cdot\underline{\nabla}_t^*\theta + v_n \frac{\partial\theta}{\partial n}\right\} = \left\{\frac{\partial^2\theta}{\partial n^2} + \frac{l}{l_c}\frac{\partial\theta}{\partial n}c + \right.$$

$$\left. + l^2\underline{\nabla}_t^*\cdot\underline{\nabla}_t^*\theta + P_r\frac{\bar{N}}{l_T}\varphi\right\}$$

where:

$$\bar{\underline{\omega}}_t = \frac{\partial\underline{v}_t}{\partial n} + \frac{l}{l_c}\underline{v}_t\cdot\underline{\underline{C}} - l^2\underline{\nabla}_t^* v_n \ ; \ \omega_n = \underline{\nabla}_t^*\cdot\left(\underline{v}_t\wedge\underline{n}\right) \qquad (7.11)$$

$$\frac{1}{2}\varphi = \frac{1}{2}\bar{\underline{\omega}}_t\cdot\bar{\underline{\omega}}_t + l^2\left(\frac{\partial v_n}{\partial n}\right)^2 + l^2\left[\left(\underline{\nabla}_t^*\underline{v}_t\right)^s_t + \frac{l}{l_c}v_n\underline{\underline{C}}\right]:\left[\left(\underline{\nabla}_t^*\underline{v}_t\right)^s_t + \frac{l}{l_c}v_n\underline{\underline{C}}\right]$$

The Reynolds, Grashoff, Peclet and Prandtl numbers, the hydrostatic and dynamic Eckert numbers, the number β and the kinetic number N are defined by:

$$\bar{R}_e = \frac{V_r L}{\nu} \ ; \ \bar{G}_r = \frac{\beta L^2 g}{\nu V_r} \ ; \ P_e = P_r R_e \ ; \ \bar{E}_h = p_{hr}/\rho_0 V_r^2$$

$$\bar{E} = p_r/\rho_0 V_r^2 \ ; \ P_r = \frac{\nu}{\alpha} \ ; \ \beta = \beta_T(\Delta T)_r \ ; \ N = V_r^2/c_p(\Delta T)_r \qquad (7.12)$$

When needed, a subscript (i) will be used to identify numbers and properties of the i-th fluid.

7.3.2 Surface field equations

Surface balance equations involve scale factors and transport properties of both volume phases. The properties of fluid

labelled one are used to put the balance equations in non-dimensional form.
Characterization of fluid labelled (1) depends on the problem considered and must be determined from the order of magnitude analysis.

The non-dimensional form of the surface balance equations are:

$$\frac{1}{l_c}\left(1 - C_\sigma l_T\theta\right)k + \bar{C}_{r1}\, 2\,\underline{\nabla}_t^*\cdot\underline{v}_1\, \delta\left(\frac{\mu}{\mu_1}\right) + \bar{W}_h l_t\, \delta\pi_h + l_p l_t\, \delta\left(\bar{W}\pi\right) = 0$$

$$\bar{M}a_1\, l_1 l_T \underline{\nabla}_t^*\theta_1 - \delta\left[\frac{l_1}{l}\frac{\mu}{\mu_1}\frac{\partial\underline{v}_t}{\partial n}\right] + \frac{l_1}{l_c}\underline{v}_1\cdot\underline{\underline{b}}\ \delta\left(\frac{\mu}{\mu_1}\right) = 0 \qquad (7.13)$$

$$\delta\left[\frac{l_1}{l}\frac{\lambda}{\lambda_1}\frac{\partial\theta}{\partial n}\right] = \left[1 + \frac{(\Delta T)_r}{T_0} l_T\theta_1\right]\frac{T_0}{l_T(\Delta T)_r}\bar{M}a_1\, P_{r1}\, \bar{N}_1\, l_1\, \underline{\nabla}_t^*\cdot\underline{v}_1$$

The Marangoni number (Ma_1), the crispation number (Cr_1), the hydrostatic ($\overline{Wh}$) and dynamic ($\bar{W}$) Weber numbers and the number C_σ are defined by:

$$\bar{M}a_1 = \frac{\sigma_T(\Delta T)_r}{\mu_1 V_r} \ ; \ C_{r1} = \frac{\mu_1 V_r}{\sigma_0} \ ; \ \bar{W}_h = p_{hr}L/\sigma_0$$

$$\bar{W}_i = p_{ri}L/\sigma_0 \quad (i = 1,2) \ ; \ C_\sigma = \sigma_T(\Delta T)_r/\sigma_0 \qquad (7.14)$$

where the subscript one indicates that the number is defined in terms of properties of fluid one.

The non-dimensional form of the remaining surface field equations reads simply:

$$V_n(n = 0^{\pm}) = 0 \; ; \quad \delta \underline{v}_t = 0 \; ; \quad \delta\theta = 0 \qquad (7.15)$$

No meaning can be as yet ascribed to the non-dimensional numbers defined by eqs. (7.12) and (7.14).

The reason is two-fold. Firstly they involve, with the exception of C_g, still undetermined reference quantities (V_r, $P_{\ell s}$, P_{ti}). Secondly they are always combined, in the field equations, with one or more scale factors (l_T, l_t, l_p, l) equally still undetermined.

Not all above numbers are indipendent since the following equalities hold:

$$\overline{W} = \overline{Re}\,\overline{E}\,\overline{Gr} \; ; \qquad \overline{Gr}_i \cdot \overline{Ma}_i = C_\sigma \qquad (7.16)$$

Eliminating Vr among the numbers $\overline{Gr}_i$ and $\overline{Ma}_i$ yields:

$$\frac{\overline{Gr}_i}{\overline{Ma}_i} = \frac{\beta_i L^2 g \rho_i}{\sigma_T (\Delta T)_2} \Rightarrow \frac{\overline{Gr}_i}{\overline{Ma}_i \hat{B}_{oi}} = \frac{\beta_i \sigma_o}{\sigma_T (\Delta T)_2} = \left(\frac{d \ln \rho}{d \ln \sigma}\right)_p \qquad (7.17)$$

where:

$$\hat{B}_o = L^2 \rho g / \sigma_o$$

The number on the right side of eq. $(7.17)_2$ depends only on fluid properties. The grouping of numbers on the l.h.s. is thus independent of geometrical factors, imposed temperature gradients and gravitational levels.

7.4 HYDROSTATIC FIELD EQUATIONS

The hydrostatic field equations yield a useful example for the proper application of a corrent o.m. analysis and, in addition, can be conveniently used to eliminate the hydrostatic contribution from the field equations.

When setting $\underline{v} = \underline{0}$; $\Theta = 0$; $\pi = 0$ equations (7.10) and (7.13) reduce, on account of the definitions (7.12) and (7.14) to

$$\frac{\partial \Pi_h}{\partial n} = \frac{\rho_o g \ell L_t}{p_{hr}} \hat{\underline{g}} \cdot \underline{n} = \frac{\rho_o g L_n}{p_{hr}} \hat{\underline{g}} \cdot \underline{n}$$

$$\underline{\nabla}_t^* \Pi_h = \frac{\rho_o g L_t}{p_{hr}} \hat{\underline{g}}_t \qquad (7.18)$$

$$-K_h = \frac{L_c p_{hr}}{\sigma_o} S \Pi_h$$

where K_h is the mean curvatwre of S. The last equation indicates that the proper reference pressure:

$$p_{hr} = \frac{\sigma_o}{L_c} \qquad (7.19)$$

is to be defined in terms of L_c which, as said, is of the order of the smallest principal radius of curvature of the interface.

Multiply eq. $(7.18)_1$ by $\underline{n}/\ell$ add it to eq. $(7.18)_2$ account for the last equation (7.9) and integrate to obtain, on account of eq. (7.13):

$$H_h - H_{ho} = \frac{\rho_o g L_T L_c}{\sigma_o} (z_o - z) \qquad (7.20)$$

where Z is the non-dimensional coordinate in the direction of $(-\hat{\underline{g}})$, and Z_o a suitable reference level where $H_h = H_{ho}$.

If

$$Z_s = F(\eta^1, \eta^2) \qquad (7.21)$$

is the equation of the interface in the coordinate system (Z, η^1, η^2), substituting the jump of eq. (7.20) on S into eq. $(7.18)_3$ and accounting for eq. (7.19) lead to the non-dimensional and properly normalized form of the Laplace equation:

$$K_h + \delta H_{ho} = \delta B_o \bar{Z}_s \qquad (7.22)$$

where

$$\bar{Z}_s = \frac{Z_s - Z_o}{L_g} L_t \quad ; \quad L_g = \max |Z_s - Z_o| L_t$$

$$(7.23)$$

$$\delta B_o = B_{ok} \frac{\delta \rho_o}{\rho_{ok}} \quad ; \quad B_{ok} = \frac{L_g L_c \rho_{ok} g}{\sigma_o}$$

and the subscript (k) denotes quantities pertaining to the heavier fluid.

Eq. $(7.23)_4$ gives the only correct definition of the hydrostatic Bond number, measuring the relative importance of leading "capillarity" and hydrostatic pressures. This definition properly accounts for the vectorial character of the force responsible for the variations of hydrostatic pressure. The length L_g characterizes the extension of the interface in the direction of $\underline{g}$. L

[(Z_o on interface) or its maximum distance from the equipotantial surface $z = z_o$ (z_o not on interface and $\delta H_{ho} = 0$)].
L_c characterizes the smallest principal radius of curvature of the interface which, in general, is in a direction different from that of L_g.

Eq. $(7.23)_3$ explains the hydrostatic zero-g simulations by means of Plateau configurations ($\delta \rho_o = 0 \Rightarrow \delta B_o = 0$).

A thorough discussion of the solutions of the Laplace equation (7.22) requires the formulation of appropriate boundary conditions and is outside the scope of the present paper. In the form derived here it does provide however a simple yet significant example of the kind of a-priori information that one can obtain from a correct application of order of magnitude analyses and of the role played by the length scale factors. To deduce a-priori information L_g and L_c must be expressed in terms of a known geometrical length L of the problem by means of scale factors: $L = l_g L$; $L_c = l_c L$. Denote by δB_{oL} the jump of the Bond number based on L. Then:

$$\delta B_o = \delta B_{oL} l_g l_c \qquad (7.24)$$

with δB_{oL} known a-priori. When $\delta B_{oL} << 1$, l_g and l_c are irrelevant and can be taken equal to one: gravitational effects are negligible and the mean curvature of the interface is constant. When $\delta B_{oL} = 0(1)$, l_g and l_c can be used to further normalize the Laplace equation by taking $\delta B_o = 1$; i.e.

$$\frac{g L_g L_c \delta \rho_o}{\sigma_o} = 1$$

(Upon modifying the reference pressure by letting $\delta H_{ho} = \pm 1$, the Laplace equation can be fully normalized to read $K_h \pm 1 = \bar{Z}_s$, a form which lends itself to interesting "similarity" consideration).

When $\delta B_{oL} >> 1$ eq. (7.22) yields, formally, the solution $\bar{z}_g = 0$ (the interface is an equipotential surface). This solution either makes no sense or, when it does (as in plane problems), is not uniformely valid. In both cases lg and lc cannot be both of order one but must be determined from the condition $\delta B_o = \delta B_{oL}\, \ell_g \ell_c =$ 1 (which, in plane problems, characterizes the extension of regions near solid boundaries where gravitational and capillarity pressure effects balance out).

A proper formulation of the o.m. analysis provides therefore the following important a-priori information. The product $L_g\, L_c$ of the length characterizing the geometry of the interface (L_c) and its maximum extension in the direction of the gravity field can at most be of the same order of magnitude as ($L_b^2\, \rho_{oK} / \delta\rho_o$) where $L_b = \sqrt{\sigma_o / \rho_{oK}\, g}$ is the Bond characteristic length (also known as capillary constant) of the heavier fluid. [This maximum o.m., being based on equilibrium considerations only, may be further limited by stability considerations].

This criterion provides a-priori estimates for the maximum extension L_g of the interface in the direction of the gravity field when L_c is either known (e.g.: sessile drops menisci in pipes, having drops floating zones) or is the same order of L_g (e.g. wall menisci).

Next paragraphs will show the wealth of similar a-priori information that the correct application of o.m. analysis can yield in flow problems.

When static contributions are eliminated from the field equations the body force terms must be replaced by the buoyancy terms:

$$\ell_t^2\, \ell_T\, \ell^3\, \bar{G}_r\, \Theta\, \underline{\hat{g}} \cdot \underline{n} \quad ; \quad \ell_t^2\, \ell_T\, \ell^2\, \bar{G}_r\, \Theta\, \underline{\hat{g}}_t \qquad (7.25)$$

in the normal and tangential volume momentum equations, respectively. The hydrostatic jump term in the surface normal momentum equation must be replaced by ($- K_h$) which, according to equation (7.22), is eiher constant or function of the coordinate $\bar{z}_g$ in the ($- \hat{\underline{g}}$) direction.

In this latter case the jump $\delta \Pi_h(\eta^1, \eta^2)$ at a point $Q(\eta^1, \eta^2)$ of the "dynamic" interface is equal to the jump across the hydrostatic interface at the point Q' having the same coordinate z_g as Q. Thus, if $\bar{Z}_g^*$ denotes the value of the $\bar{Z}_g$ coordinate of Q, $K_h = k_h(\bar{Z}_g - \bar{Z}_g^*)$.

8. ORDER OF MAGNITUDE ANALYSIS

8.1 Introduction

Convection in the absence of imposed velocities or pressure gradients in fluid systems with interfaces may be classified as natural, Marangoni or combined free convection according to whether the motion is caused by buoyant forces, Marangoni stresses or both.
An order of magnitude analysis, if done properly, will provide all information a priori, i.e. in terms only of data of the problem, on the the type of convection prevailing, the nature of flow regimes, the coupling of the two fields, the order of mafnitude of the velocity, and so on.
In this chapter we propose a general order of magnitude analysis, to investigate the general case in wich the interfacing fluids, the gravity level g, the imposed temperature difference and the extension of the interface are arbitrary. Two main interrelated objectives are set forth:

i) To identify and classify systematically all possible flow regimes occuring in natural, Marangoni and combined convection
ii) To formulate the criteria that make is possible to determine a priori, in each specific case, which situation will prevail.

Space limitation impose a number of restrictions to the generality aimed at in the present work. Thus it is assumed that the geometrical lengths are all of the same order and that the flow regions near fluid solid interface do not influence, in terms of orders of magnitude, the analysis herein carried out.

8.2 Mathematical formulation

We shall only be concerned with the determination of the reference velocity Vr, and of the two scale factors l_i defining the length scales $l_i L$ in the direction notmal to the interface, where L is a geometrical length characteristic of the problem considered.
Determination of scale factors ℓ_t defining length scales $\ell_t L$ in the direction parallel to the interfaces (relevant for instance, when considering simultaneously fluid-fluid and fluid-solid interfaces) of reference pressures and of the influence of motion on the shape of fluid-fluid interfaces will not be considered. The interface will be modeled as a massless surface phase with only one intensive thermodynamic degree of freedom; surface irreversibility will be neglected and the smaller radius of curvature will be assumed to be of the same order as L. The motion is steady, volume phase linear phenomenological relations and Boussinesq approximations are used.
The balance equations to be analysed are those of:
tangential momentum for the two volume phases and for the surface phase;
internal energy for the two volume phases.
The general criteria that must be used for the determination of V_1, ℓ_1, ℓ_2 where discussed in [1] and are further elaborated in what follows:

1) The non dimensional measures of the leading diffusion terms must be set equal to one to ensure proper applicability of boundary conditions. In the volume phases the leading diffusion terms are those due to normal gradients of normal fluxes. In the surface phase tangential momentum equation the leading viscous term is not known a priori since the measure of the relative importance of the two tangential viscous stresses τ_i acting on the interface involves also the a priori unknown scale facors l_i.

2) The measure of the largest driving action must be set equal to one. In the subject case there are three driving actions: the buoyant forces in each fluid and the Marangoni stress. There are two measures of the Marangoni stress, one in terms of τ_1 and the other in terms of τ_2. The appropriate one is the smaller of the two, corresponding to the largest τ, not unknown a priori.
Both measures must therefore be introduced and the identification, in each case, of the appropriate one must follows from the order of magnitude analysis.

3) The measures of all other terms entering the balance equations must be at most of order one. Each contribution to a non dimensional balance equation is the product of two facors: one contains dimensionless field variables and their derivatives and the other is a nondimensional number. If the nondimensional process was done properly the first factor is at most of order one and the nondimensional number yield consequently an upper bound to the measure of the relative importance of the considered contribution. These numbers will be referred as measure numbers. Imposing that they be at most of order one is a sufficient condition to ensure that no contribution to the balance equation is of order higher than that of the leading diffusion term.

4) The scale factors ℓ_i must have the largest value compatible with the constraints deriving from the formulation of the preceding criteria. This will ensure the largest domain of uniform validity for the corresponding forms of the field equations.
The measure numbers to be considered in the subject case are those for tangential convection of momentum C_{m_i} and internal energy C_{e_i}, for the buoyant forces B_i for the two measures M_i of the Marangoni stress and for the ratio r_j of the two viscous stresses acting on the interface (momentum resistivity ratio). Other measure numbers appearing in the balance equations herein considered are either to be used in the determination of reference pressures or are automatically at most of order one in the subject problem.

Let σ be the interfacial tension,

$$\Delta\rho = -\rho_0 \beta_T \Delta T \,; \qquad \Delta\sigma = -\sigma_0 \sigma_T \Delta T$$

where the subscript zero denotes values in the reference state $T = T_0$ and β_T, σ_T are constant; μ_i the viscosity coefficients; ν_i, α_i the momentum and energy diffusion coefficients and let the subscript i $(i=1,2)$ denote the i-th
fluid, fluid one being the more viscous fluid. The pertinent measures numbers are given by:

$$C_{m_i} = \frac{V_r L}{\nu_i} \ell_i^2 = Re^*_i \ell_i^2 \,; \quad C_{e_i} = \frac{V_r L}{\alpha_i} \ell_i^2 = Pe^*_i \ell_i^2 \,;$$

$$B_i = \frac{|\Delta\rho|_i \, g L^2}{V_r \mu_i} \ell_i^3 = Gr^*_i \ell_i^3 \,; \quad M_i = \frac{|\Delta\sigma|}{V_r \mu_i} \ell_i = Ma^*_i \ell_i \quad (i=1,2)$$

$$r_j = \frac{\mu_j \ell_i}{\mu_i \ell_j} = \frac{M_i}{M_j} = \frac{\tau_j}{\tau_i} \qquad (i \neq j = 1,2). \tag{8.1}$$

The subscript star indicates that characteristic numbers (Reynolds, Peclet, Grashoff and Marangoni) appearing in these equations are defined in terms of the still unspecified reference velocity V_r.
On account of the previously mentioned criteria, the determination of V_r, ℓ_1, ℓ_2 for a given set of problems data can be formulated as the solution of the following constrained maximum problem:

$$\begin{aligned}
&max(\ell_i), \quad (i = 1,2): \\
&max[B_1, B_2, min(M_1, M_2)] = 1; \qquad \ell_i \leq O(1) \\
&C_{m_J} \leq O(1); \quad C_{\ell_i} \leq O(1); \quad B_i \leq O(1); \qquad (8.2) \\
&M_i \leq O(1); \quad r_J = \frac{M_i}{M_J} \leq O(1); \qquad (i \neq J = 1,2).
\end{aligned}$$

The maximum problem can be alternatively and conveniently formulated in terms of either characteristic speeds or characteristic lengths.

The definition of the starred characteristic numbers led, in an almost obvious manner to the identification of two sets of characteristic speeds depending only on problem's data:

$$\begin{aligned}
&V_{\nu_i} = \frac{\nu_i}{L}; \qquad V_{\alpha_i} = \frac{\alpha_i}{L}; \qquad (8.3) \\
&V_{g_i} = \frac{|\Delta\rho|_i g L^2}{\mu_i}; \qquad V_{m_i} = \frac{|\Delta\sigma|}{\mu_i}; \qquad (i = 1,2)
\end{aligned}$$

The four speeds of the first set are the well known momentum and energy diffusion speeds. Those of the second will be referred as driving speeds: the first two are buoyant speeds, the second two are the Marangoni speeds.

The equations[13] show that there are six independent characteristic lengths. Their choice is not unique: they must be referred to a characteristic speed independent of L and there are several alternatives available (e.g. the two Marangoni speeds; any of the combined speeds V_i^{ν} V_i^{α} obtained upon elimination of L between the diffusion and buoyant speeds). We choose to define characteristic lengths i terms of the Marangoni speeds V_{m_1} of the more viscous fluid. Thus:

$$L_{\nu_i} = \frac{\nu_i \mu_1}{|\Delta\sigma|}; \qquad L_{\alpha_i} = \frac{\alpha_i \mu_1}{|\Delta\sigma|}; \qquad L_{b_i} = \left[\frac{|\Delta\sigma| \mu_i}{g |\Delta\rho|_i \mu_i}\right]^{1/2} \quad (8.4)$$

The first four are diffusion characteristic lengths, the other two will be referred to as dynamic Bond lengths. They are related to the hydrostatic Bond length

$$L_{bh} = \left[\frac{\sigma_o}{|\rho_1 - \rho_2|_o g}\right]^{1/2}$$

by

$$\frac{L_{bi}}{L_{bh}} = \left[\frac{\sigma_T}{(\rho_T)_i} \frac{|\rho_1 - \rho_2|_o \mu_i}{\rho_{io} \mu_1}\right]^{1/2} \qquad (8.5)$$

This ratio is independent of the gravity level g, the imposed temperature difference ΔT and the length L

In terms of characteristic speeds problem the constrained maximum problem reads

$$\begin{aligned}
&max(\ell_i). \quad (i = 1,2): \quad \ell_i \leq O(1); \qquad (8.6) \\
&V_1 = max\left\{V_{g_i} \ell_i^2, min(\ell_i V_{m_i})\right\} \leq O\left[min\left(\frac{V_{\nu_i}}{\ell_i^2}, \frac{V_{\alpha_i}}{\ell_i^2}\right)\right],
\end{aligned}$$

and in terms of characteristic lengths

$$\begin{aligned}
&max(\ell_i), \quad (i \neq 1,2): \quad \ell_i \leq O(1) \\
&\qquad\qquad (8.7) \\
&\frac{V_1}{V_{m_1}} = max\left\{\frac{L^2 \ell_i^2}{L_{b_i}^2}, min\left(\ell_1, \frac{\ell_2}{\ell_1}\frac{\mu_1}{\mu_2}\right)\right\} \leq O\left[min\left(\frac{L_{\nu_i}}{\rho_i^2 L}, \frac{L_{\alpha_i}}{\rho_i^2 L}\right)\right].
\end{aligned}$$

Each solution V_1, ℓ_i, ℓ_1 correspond to a certain range of orders of magnitude of appropriate combination of problem's data. Such a range will be referred to as feasible range of the given solution.

8.3 Flow regimes

The o.m. of the convection numbers and of the scale factors determine the different regimes for the velocity and the temperature fields. The following terminology will be used.

1) Diffusive regimes ($l_1=l_2=1$)

2) Dissipative layer regimes (at least one $l_i<O(1)$) characterized by the presence of at least one dissipative layer adjacent to the interface.

8.4 Conditional characteristic numbers

The starred characteristic numbers⁴'are defined in terms of a yet unspecified reference velocity V_r and can obviously be expressed in terms of the characteristic speeds 8.3 :

$$Re^*_i = \frac{V_r}{V_{\nu i}}; \qquad Pe^*_i = \frac{V_r}{V_{\alpha i}}; \qquad (8.8)$$
$$Gr^*_i = \frac{V_{gi}}{V_r}; \qquad Ma^*_i = \frac{V_{mI}}{V_r};$$

This form evidences the different roles of diffusion and driving speeds with respect to the reference velocity (see the formulation of the max problem in terms of the characteristic speeds) and shows that the following products 'or ratios are independent of V_r:

$$Re^*_i\, Gr^*_I = \frac{V_{gI}}{V_{\nu i}} = \frac{|\Delta\rho|_I\, g L^3}{\nu_i \mu_I}; \qquad Pe^*_i\, Gr^*_I = \frac{V_{gI}}{V_{\alpha i}} = \frac{|\Delta\rho|\, g L^3}{\alpha_i \mu_I}; \qquad (8.9)$$

$$Re^*_i\, Ma^*_I = \frac{V_{mI}}{V_{\nu i}} = \frac{|\Delta\sigma| L}{\nu_i \mu_I}; \quad Pe^*_i\, Ma^*_I = \frac{V_{mI}}{V_{\alpha i}} = \frac{|\Delta\sigma| L}{\alpha_i \mu_I}; \quad \frac{Gr^*_I}{Ma^*_i} = \frac{V_{gI}}{V_{mi}} = \frac{|\Delta\rho|_I\, g L^2 \mu_i}{|\Delta\sigma| \mu_I}.$$

They are all equal to ratios of characteristic speeds: the first four involve a driving and a diffusion speed, the last one a buoyant and a Marangoni speed.

To clarify the notion of characteristic conditional numbers, consider a, number X^* defined in terms of a reference velocity V_r and a characteristic speed V_x measuring in diffusive regimes the relative importance (A/B) of two phenomena A and B and suppose that $X^*=V_r/V_x$. When V_r is equal to an imposed velocity V_∞ the characteristic number $X_\infty=V_\infty/V_x$ will be called "absolute" as it gives a measure of the two phenomena A and B independently of that of other phenomena. When there is no imposed velocity, V_r is a fortiori equal to another characteristic speed V_y. The number $X_y = X^*(V_r=V_y) = V_y/V_x$ will then be called a conditional characteristic number as it yields the measure of the relative importance of the two phenomena A and B given that the measure of two other phenomena (say C and D)is equal to one. As with the all conditional measures, a duality is involved. Let Y^* be the characteristic number measuring the relative importance of the phenomena C and D. If $Y^*=V_y/V_r$ then $X^*Y^*=Z=V_y/V_x$ and $X_y=X^*(V_r=V_y)=Y_x=Y^*(V_r=V_x)=Z$. That is: the number Z can be equivalently interpreted as the conditional characteristic number X_y (measure of A/B given that C and D have the same importance). Similarly, if $Y'=(V_r/V_y)$ then the number $Z'=X^*/Y^*$ is equal to either X_y or $1/Y_x$. Notice that for $V_r=V_\infty$ whereas it is still true that $Z=X^*Y^*=X_\infty Y_\infty$, the number Z cannot be considered a conditional number since X_∞ and Y_∞, being absolute numbers, have well defined values which are, in general, not equal to one. The same remarks obviously apply to Z'.

Conditional characteristic numbers will be denoted with a subscript indicating which measure is equal to one. Thus, for instance, with reference to the numbers (8.9) we have.

$$\frac{|\Delta\sigma| L}{\alpha_1 \mu_1} = \frac{V_{m1}}{V_{\alpha 1}} = Pe_{1,m_1} = Ma_{1,P_1}$$

and the implication of the duality is evident. This conditional measure can be considered as the conditional Peclet number defined i terms of the Marangoni speed (measure of the relativer importance between convection and diffusion of energy given that the Marangoni stress is of the same order of magnitude as the viscous tangential stress) or as the conditional Marangoni number defined in terms of the energy diffusion speed (measure of the relative importance between Marangoni and tangential viscous stress given that energy convection is of the same order as energy diffusion in the bulk fluid).

8.5 Analysis

An inequality will be called controlling when it implies another inequality of the same type. The controlling convection inequality in the ith fluid is determined by the largest convection measure which zill be denoted by Ci, and corresponds to the smallest of the two diffusion coefficients ν_i and α_i. To unify the treatment, we shall denote by Di the smallest diffusion coefficient and by Vd_i, X_i^* the corresponding diffusion velocity and starred transport number. The ratio $(D_2/D_1)= Vd_2/Vd_1$ will be denoted by D_{21}.

In the subject case, the scale factors are determined, independently of the value of V_r by the controlling convection inequalities. Two alternative are possible for each l_i. The value of L_i is equal to its absolute maximum (l_i=1) provided that $C_i <= O(1)$, or otherwise determined by

the condition that the controlling canvection measure be kept at its maximum allowable value (C_i=1) so that

$$l_i = \sqrt{(V_{d_i}/V_*)} < O(1).$$

The four combinations of the two possible alternatives for each scale factor determine four classes of solutions of the max problem2which are listed in table 1. The first class correspond to diffusive regimes, the other three to dissipative layer regimes with the l_i giving, when of order less than one, the order of magnitude of the nondimensional thickness of the layers. These thickness vary always as the inverse sqare root of the appropriate starred transport number (Reynolds or Peclet).

When two dissipative layers are present (class II) the ratio of the two thickness is independent of V_r and is always equal to the square root of the diffusivity ratio D_{21}. This generalizes a well known result holding for classical boundary layers.

The number of different solutions pertaining to each of the above four classes depend on the possible values of Vr as determined by the largest driving action. For l_2=1, the last of eqns (7.1) shows that the appropriate measure of the Marangoni stress is always M_1 [illegible] since $l_1 <= O(1)$ and upon the chosen characterization of the fluid one. There are thus three different solutions, corresponding to B_i=1 (i=1 or 2) and M_1=1, for classes I and III and four (B_i=1, M_i=1) for classes II and IV, for a total of 14.

They are listed in table 2. For dissipative layer regimes the first column gives the expression of V_r in terms of driving speeds and of scale factors, the second and third columns gives the expression for l_1 and l_2 and the last column gives the final expression for Vr. Dissipative layers will be called buoyant or Marangoni layers according to whether the leading driving action is due to buoyant forces or to Marangoni stress, respectively.

Table 2 evidences a number of important points that are worth stressing.

1) In diffusive regimes the reference velocity V_r is always equal to a driving characteristic speed.

2) The law of variation of dissipative layers thickness with the inverse of the appropriate conditional transport number may be the well known one-fourth law (buoyant layers), the one-third law (Marangoni layers) or also the classical one-half law .

   The present approach to the analysis of dissipative layers provides a clear physical explanation for these different laws. As already pointed out, dissipative layers always vary as the inverse square root of starred transport numbers, defined in terms of the reference velocity V_r. The classical one-half law prevails when V_r is either equal to an imposed velocity (classical dissipative layers) or to a driving characteristic speed (buoyant or Marangoni layers only on one side of the interface). The other laws prevail when V_r is smaller than a driving characteristic speed. The second column of table 2 shows that in these cases V_r is equal to $V_F \chi^p$ where V_f is a driving characteristic speed and the exponent p depends on its nature. For V_f equal to a buoyant speed $p=2$ and the one-fourth law is obtained; for V_f equal to a Marangoni speed $p=1$ and the one-third law is obtained.

3) The 1/2 power law prevails if there is only one dissipative layer on one side of the interface while the driving action is due to the fluid on the other side of it
As a consequence, the dissipative layers behaves as any shear layers caused by an imposed velocity on one of its borders and thus the 1/2 power law holds.

4) A necessary condition for V_r to differ from a driving speed V_f is that at least one dissipative layer be present. V_r is then smaller than V_f and equal to V_f divided by the square root (buoyant layers) or the cubic root (Marangoni layers) of the appropriate conditional transport number. V_r can also be expressed as a the weighed geometrical mean between a driving and a diffusion speed. For buoyant layers both weights are equal to one-half, for Marangoni layers, the weight of the Marangoni speed is two thirds and that of the diffusion speed is one third .

5) The driving and diffusion speeds characterizing the expression of conditional transport numbers pertain to a same fluid for layers following the 1/4 or 1/3 power law and the two different fluids for layers following the 1/2 power law. In this latter case only three of the possible four transport numbers are involved since, as already mentioned, for $l_2=1$ the appropriate measure of the Marangoni stress is M_1 and consequently, V_r can never be equal to V_{M2}.

The numbers X_{igi} will be referred to as the (conditional) Grashoff or Rayleigh numbers, as appropriate.
The more coherent terminology will be used for the other numbers which will be called conditional Reynolds and Peclet numbers, as appropriate. When needed, the speeds entering their definition will be mentioned explicitely. For ease in writing the numbers $X_{1,Mi}$ will be simple denoted by Re_M or Pe_M as appropriate and, likewise, the numbers X_{igi} will be denoted by G_{ri} or R_{ai}.

8.6 Feasible ranges

The problem's data are: the temperature difference ΔT, the length L (in the present particular case the other geometrical lengths are supposed to be of the same order of magnitude as L and thus are not relevant for the o.m. analysis), the gravity level g/g_0 where g_0 is the heart gravity, the physical properties of the two fluids and of their interface. The feasible ranges for the sets of solutions listed in tables 2 are expressed in terms of the orders of magnitude of appropriate combinations of these problem's data, hereinafter referred to as parameters.
For $l_1=l_2=1$ (diffusive regimes) the feasible range is determined by the condition that the largest driving speed V_D be at most of the same order as the smallest diffusion speed Vd since equations $(7.6)_3$ reduce to $V_r = V_D <= V_d$.
As the measure numbers coincide with the starred characteristic numbers, the relevant parameters are given by the seven independent ratios that can be formed with the eight characteristic speeds given by eqns (8.3) .
Five of them, involving only the properties of the fluids, are:

$$Pr_i = \frac{V_{\nu i}}{V_{d i}} = \frac{L_{\nu i}}{L_{d i}}; \qquad D_{21} = \frac{V_{d2}}{L_{d1}} = \frac{L_{d2}}{L_{d1}};$$

$$G_{21} = \frac{|\Delta\rho|_{21}}{\mu_{21}} = \frac{V_{g2}}{V_{g1}} = \frac{L_{b1}^2}{L_{b2}^2}; \qquad \mu_{21} = \frac{V_{m1}}{V_{m2}} \le O(1); \tag{8.10}$$

where $f_{ij}=f_i/f_j$ and Pr is the Prandtl number.
The other two parameters involve also L, g, ΔT.
Several choices are possible and we shall find useful to use the following one:

$$\frac{G_{ri}^*}{Ma_1^*} = \frac{|\Delta\rho|_i g L^2 \mu_1}{\mu_i |\Delta\sigma|} = \frac{V_{gi}}{V_{m1}} = \frac{L^2}{L_{bi}^2}; \quad X_1^* Ma_1^* = X_{1,m} = \frac{|\Delta\sigma| L}{\mu_1 D_1} = \frac{V_{m1}}{V_{d1}} = \frac{L}{L_{d1}} \tag{8.11}$$

which coincides with two of the combinations of starred numbers given by eqns (8.9).
The properties of the fluid identify the smallest diffusion speed (denoted as V_{dl}) and the largest buoyant speed (denoted as Vgk). $V_{d\ell}$ is determened by the o.m. of the Prandtl numbers ($D_i = \nu_i$ for $P_{ri} <= O(1)$ and $D_i = \alpha_i$ for $P_{ri} > O(1)$) and of the diffusivity ratio D_{21}. V_{gk} is determined by the o.m. of the parameter G_{21}. To determine the largest driving speed and to evaluate the inequality ($V_D <= V_d$) also the other problem's data must be prescribed. V_D is equal to either V_{gk} or V_{M1}. The alternative depends on the o.m. of the first parameter (8.11) a fact which justifies having called L_{bi} the dynamic Bond length. For $L << L_{bk}$ buoyant effects are negligible ($V_{gk} << V_{M1}$; $V_r = V_{M1}$), for $L >> L_{bk}$ Marangoni effects are negligible ($V_{gk} >> V_{M1}$; $V_r = V_{gk}$) and for $L = L_{bk}$ both effects are equally important ($V_{gk} \simeq V_{M1}$; $V_r = V_{gk} \simeq V_{M1}$).
The inequality $V_D <= V_d$ reads $X_{gk} \le O(1)$ or $X_{1,m} \le O(1)$ according to whether $V_D = V_{gk}$ or $V_D = V_{M1}$ and together with those leading to the identification of V_D and V_d, determine the feasible ranges of the three different solutions for diffusive regimes ($V_r = V_{g1}$, V_{g2} or V_{M1})
For the other regimes (at least one l_i different from one) the measure numbers (8.1) must be considered. Elimination of V_r, ℓ_1, ℓ_2 from eqns (8.1) yields five independent ratios that are conveniently chosen to be given by the set:

$$Pr_i = C_{mi}/C_{ei};$$

$$\frac{\mu_{21}}{\sqrt{D_{21}}} = \frac{M_1}{M_2}\sqrt{\frac{C_2}{C_1}}; \qquad G_{21} D_{21} = \frac{C_1}{C_2}\frac{B_2}{B_1}; \tag{8.12}$$

$$\frac{V_{g1}}{V_{m1}}\left(\frac{V_{d1}}{V_{m1}}\right)^{1/3} = \left(\frac{L}{L_{b1}}\right)^2\left(\frac{L_{d1}}{L}\right)^{1/3} = \frac{B_1}{C_1^{1/3} M_1^{4/3}} \tag{8.13}$$

Three additional useful relations are obtained upon elimination of V_r and l_1 from among the B_i's C_i's M_i's

$$\frac{C_2}{C_1} = \frac{\ell_{21}^2}{D_{21}}; \quad \frac{B_2}{B_1} = G_{21}\ell_{21}^2; \quad \frac{M_1}{M_2} = \ell_2 = \frac{\mu_{21}}{\ell_{21}} \tag{8.14}$$

Only one of them is independent, the other two following from equations 8.12. Equations 8.12 and 8.14 show that:

1) Obviously, the smallest diffusion speed is still determined by the fluid properties only.

2) The necessary conditions for the validity of solutions pertaining to classes III and IV are $D_{21} > O(1)$ and $D_{21} < O(1)$, respectively.

3) The appropriate measure of the Marangoni force and the controlling buoyancy inequality are almost always determined by the fluid properties only. However the relevant parameters are now $\mu_{21}/\sqrt{D_{21}}$ and $G_{21} D_{21}$.

The situation as deduced from eqns ^{4} for class II , and from eqns $(8.12)_{2,3}$ and 8.14 for classes III and IV, is summarized in Table 3 wherein class I has also be included, for ready comparison. When both B_i or both M_i appear it means that the controlling buoyancy inequality or the appropriate measure of the Marangoni stress do not depend on fluid properties only. This occurs in three cases pertaining to classes III and IV. As in diffusive regimes, the other problem's data are then needed for the final determination of the largest driving force.

Table 3 suggest a convenient method for a compact representation of all possible solutions and of their feasible ranges. As seen, there are seven independent parameters, five of which depend only on the properties of the fluid. It is possible therefore to partition all possible couples of fluids into a number of classes defined by the appropriate combinations of the orders of magnitude of the fluid parameters. To each such class there corresponds a subset of the solutions listed in table 2 , identified by the orders of magnitude of the remaining two parameters, which define a plane. The feasible ranges corresponding to these solutions span this plane and thus provide a compact representation of all possible solutions pertaining to any couple of fluids belonging to the class considered.

The five parameters depending only on fluid properties are μ_{21}, Pr_i, D_{21} and G_{21}.

By definition of fluid one, μ_{21} is always<=O(1). The four relevant combinations of the o.m. of the Prandtl numbers identify, as seen, the four possible expressions for the ratio D_{21}, between the smallest diffusivity coefficients of each fluid. As to the two parameters D_{21} and G_{21}, is not sufficient to consider only two alternatives for their order of magnitude (<=O(1) and >O(1)) since the classes II, III and IV are also affected by the o.m. of the parameters $\mu_{21}/\sqrt{D_{21}}$ and $G_{21}D_{21}$.

Since:

i) $\mu_{21} \leq O(1)$ and $D_{21} \geq O(1)$ imply $\mu_{21}/\sqrt{D_{21}} \leq O(1)$;

ii) $D_{21} \geq O(1)$ and $G_{21}D_{21} \leq O(1)$ imply $G_{21} \leq O(1)$;

iii) $D_{21} \leq O(1)$ and $G_{21}D_{21} > O(1)$ imply $G_{21} > O(1)$

it follows that for each parameter D_{21} and G_{21} three alternatives need to be considered.

The number of classes in which the possibles couples of fluids must be partitioned is thus 9 if one convenes that couples of fluid with the same o.m. of D_{21} belong to a same class whichever is the actual expression for D_{21}, i.e. whichever is the o.m. of the Prandtl numbers of the two fluids.

It proves convenient to express orders of magnitude in terms of powers of a small parameter $\varepsilon \ll 1$ whose degree of smallness characterizes the separation between consecutive orders of magnitude. We thus let:

$$\mu_{21} = \varepsilon^{\mu}; \quad D_{21} = \varepsilon^{d_{21}}; \quad \mu_{21}/\sqrt{D_{21}} = \varepsilon^{d};$$
$$G_{21} = \varepsilon^{g_{21}}; \; G_{21}D_{21} = \varepsilon^{g}; \quad \left[d = \mu - \frac{d_{21}}{2}; \; g = d_{21} + g_{21}\right]. \qquad (8.15)$$

The nine fluid classes correspond to the different relevant alternatives as to the signs of d_{21}, g_{21}, d and g. They are listed in Table 4 together with the subset of solutions belonging to each class.

A given couple of fluids can, in principle, belong to any one of the above nine classes. To get an idea of the situation prevailing with fluids of potential interest in microgravity applications, the following classes have been considered: liquid metals, organic liquids, molten salts, silicon oils, water (pure and contaminated), typical natural wax, typical molten glass. Ranges of orders of magnitude of the different relevant parameter for liquid-air systems are listed in Table 4b.

The other two parameters entering the definition of feasible ranges are chosen to be the speed ratios:

$$\frac{V_{m1}}{V_{d1}} = \frac{L}{L_{d1}} = X_{1m} = \varepsilon^{m_1}; \quad \frac{V_{g1}}{V_{m1}} = G_{rm} = \varepsilon^{g_1}; \qquad (8.16)$$

They are two conditional characteristic numbers. The first one is either Re_M or Pe_M according to whether Pr_1<=O(1) or Pr_1>O(1). The product of the numbers (8.16) is correspondingly the conditional Grashoff or Rayleigh number of the more viscous fluid.

The feasible ranges for the solutions listed in table 2 are readily found by sobstituting the given expressions for V_r, ℓ_1, ℓ_2 in the inequalities (8.2) and by expressing them in terms of the exponents defined by equations (8.15) and (8.16).

Results are summarized in table 5 which gives, for each case:

- the considered solutions, as identified by the numbers used in table 2 and by those used in Figs.2;

- the unitary measure identifying the largest driving force;

- the inequalities (controlling or not corresponding to the other measure numbers;

- the scale factors l_i and the reference velocity V_r.

For each of the solutions III1, IV1, II2, and IV2, pertaining to natural or combined convection, there are also shown the two ranges corresponding to the two different measures (M_1 or M_2) of the Marangoni stress and thus identifying the largest shear stress acting on the interface.

Table 1. Classes of solutions for scale factors

	C_1	C_2	l_1	l_2
I	$\leq O(1)$	$\leq O(1)$	1	1
II	1	1	$\sqrt{\frac{V_{d1}}{V_r}} = \frac{1}{\sqrt{X_1^*}}$	$\sqrt{\frac{V_{d2}}{V_r}} = \frac{\sqrt{D_{21}}}{\sqrt{X_1^*}} = \frac{1}{\sqrt{X_2^*}}$
III	1	$\leq O(1)$	$\sqrt{\frac{V_{d1}}{V_r}} = \frac{1}{\sqrt{X_1^*}}$	1
IV	$\leq O(1)$	1	1	$\sqrt{\frac{V_{d2}}{V_r}} = \frac{1}{\sqrt{X_2^*}}$

Table 2. List of the 14 different solutions for (Vr, l_1, l_2)

I	$l_1 = l_2 = 1$; 1) $V_r = V_{g1}$; 2) $V_r = V_{g2}$; 3) $V_r = V_{m1}$			
II	V_r	$l_1 = \sqrt{V_{d1}/V_r}$	$l_2 = l_1\sqrt{D_{21}} = \sqrt{V_{d2}/V_r}$	V_r
1)	$V_{g1}\,l_1^2$	$(V_{d1}/V_{g1})^{1/4} = X_{1,g1}^{-1/4}$	$\sqrt{D_{21}}\ (X_{1,g1})^{-1/4}$	$(V_{g1}V_{d1})^{1/2} = V_{g1}/\sqrt{X_{1,g1}}$
2)	$V_{g2}\,l_2^2$	$\left(\frac{V_{d1}}{V_{g2}D_{21}}\right)^{1/4} = \frac{X_{2,g2}^{-1/4}}{\sqrt{D_{21}}}$	$(V_{d2}/V_{g2})^{1/4} = X_{2,g2}^{-1/4}$	$(V_{g2}V_{d2})^{1/2} = V_{g2}/\sqrt{X_{2,g2}}$
3)	$V_{m1}\,l_1$	$(V_{d1}/V_{m1})^{1/3} = X_{1,m1}^{-1/3}$	$\sqrt{D_{21}}\ (X_{1,m1})^{-1/3}$	$V_{m1}^{2/3}V_{d1}^{1/3} = V_{m1}/X_{1,m1}^{1/3}$
4)	$V_{m2}\,l_2$	$\left(\frac{V_{d1}}{V_{m2}\,D_{21}}\right)^{1/3} = \frac{X_{2,m2}^{-1/3}}{\sqrt{D_{21}}}$	$(V_{g2}/V_{m2})^{1/3} = X_{2,m2}^{-1/3}$	$V_{m2}^{2/3}\,V_{d2}^{1/3} = V_{m2}/X_{2,m2}^{1/3}$
III	V_r	$l_1 = \sqrt{V_{d1}/V_r}$	$l_2 = 1$	V_r
1)	$V_{g1}\,l_1^2$	$X_{1,g1}^{-1/4}$	1	$V_{g1}/\sqrt{X_{1,g1}}$
2)	V_{g2}	$(V_{d1}/V_{g2})^{1/2} = X_{1,g2}^{-1/2}$	1	V_{g2}
3)	$V_{m1}\,l_1$	$X_{1,m1}^{-1/3}$	1	$V_{m1}/X_{1,m1}^{1/3}$
IV	V_r	$l_1 = 1$	$l_2 = \sqrt{V_{d2}/V_r}$	V_r
1)	V_{g1}	1	$(V_{d2}/V_{g1})^{1/2} = X_{2,g1}^{-1/2}$	V_{g1}
2)	$V_{g2}\,l_2^2$	1	$X_{2,g2}^{-1/4}$	$V_{g2}/\sqrt{X_{2,g2}}$
3)	V_{m1}	1	$(V_{d2}/V_{m1})^{1/2} = X_{2,m1}^{-1/2}$	V_{m1}
[illegible]	[illegible]	[illegible]	[illegible] $^{-1/3}$	[illegible] $^{1/3}$

Table 3.

Determination of controlling buoyancy inequality $B_i \le O(1)$					
Fluid Parameters		Classes of Solutions			
$G_{21}D_{21}$	G_{21}	I	II	III	IV
		$l_1=l_2=1$	$C_1=C_2=1$	$C_1=1$, $l_2=1$	$C_2=1$, $l_1=1$
$\le O(1)$	$\le O(1)$	B_1	B_1	B_1^{*}	B_1^{**}
	$> O(1)$	B_2		×	B_1, B_2
$> O(1)$	$\le O(1)$	B_1	B_2	B_1, B_2	×
	$> O(1)$	B_2		B_2^{**}	B_2^{*}

* From $B_2/B_1=(C_2/C_1)\,G_{21}D_{21}$; $C_i \le O(1)$; **From $B_2/B_1=G_{21}(l_2/l_1)^2$ $l_i \le$ O(1

Determination of the measure M_i for the Marangoni stress					
Fluid Parameters		Classes of Solutions			
$\mu_{21}/\sqrt{D_{21}}$	D_{21}	I	II	III	IV
		$l_1=l_2=1$	$C_1=C_2=1$	$C_1=1$; $l_2=1$	$C_2=1$; $l_1=1$
$\le O(1)$	$< O(1)$	M_1	M_1	×	M_1^{*}
	$\ge O(1)$			M_1^{**}	×
$> O(1)$	$< O(1)$		M_2	×	M_1, M_2

* From $M_1/M_2=\sqrt{C_1/C_2}\,\mu_{21}/\sqrt{D_{21}}$; $C_i \le O(1)$; **From $M_1/M_2=\mu_{21}\,l_1/l_2$; $\mu_{21} \le O(1)$ $l_i \le O(1)$

Table 4(a). Relevant different cases for o.m. of fluid's parameters

	$D_{21}=\varepsilon^{d_{21}}$	$\frac{\mu_{21}}{\sqrt{D_{21}}}=\varepsilon^{d}$	$G_{21}D_{21}=\varepsilon^{g}$	$G_{21}=\varepsilon^{g_{21}}$	Solutions (See TABLES II, V)	
A_1	$d_{21} \le 0$	$d \ge 0$	$g \ge 0$	$g_{21} \ge 0$	$(1, 2', 2)$ I3, II3, III3	$(3, 3', 4)$ I1, II1, III1
A_2			$g < 0$	$g_{21} \ge 0$		$(5, 5'', 3', 4)$ I1, II2, III1, III2
A_3				$g_{21} < 0$		$(5, 5'', 6)$ I2, II2, III2
B_1	$d_{21} > 0$	$d \ge 0$	$g \ge 0$	$g_{21} \ge 0$	$(1, 2'', 2)$ I3, II3, IV3	$(3, 3'', 4)$ I1, II1, IV1
B_2				$g_{21} < 0$		$(3, 3'', 5', 6)$ I2, II1, IV2, IV1
B_3			$g < 0$	$g_{21} < 0$		$(5, 5', 6)$ I2, II2, IV2
C_1	$d_{21} > 0$	$d < 0$	$g \ge 0$	$g_{21} \ge 0$	$(1, 2'', 2'_2, 2_2)$ I3, II4, IV3, IV4	$(3_2, 3''_2, 3'', 4)$ II1, IV1, I1
C_2				$g_{21} < 0$		$(3_2, 3_2, 3'', 5_2, 5', 6)$ I2, II1, IV1, IV2
C_3			$g < 0$	$g_{21} < 0$		$(5_2, 5'_2, 5', 6)$ I2, II2, IV2.

Table 4(b). Orders of magnitude of relevant parameters for liquid-air systems

MATERIALS	G_{21}	$(Gr_M)_{max}$	$Pr_1 \le O(1)$; $D_{21}=\nu_{21}$				$Pr_1 > O(1)$; $D_{21}=\alpha_{21}$			
			D_{21}	$\mu_{21}/\sqrt{D_{21}}$	$G_{21}D_{21}$	L_{d_1}/L_{b_1}	D_{21}	$\mu_{21}/\sqrt{D_{21}}$	$G_{21}D_{21}$	L_{d_1}/L_{b}
LIQUID METALS	$10^{-1}+10^{0}$	10^{-1}	$10^{1}+10^{2}$	$10^{-4}+10^{-2}$	$10^{1}+10^{2}$	$10^{-5}+10^{-3}$	—	—	—	—
ORGANIC LIQUIDS	$10^{-1}+10^{0}$	10^{-1}	10^{1}	$10^{-3}+10^{-2}$	$10^{0}+10^{1}$	$10^{-4}\div10^{-3}$	10^{2}	10^{-4}	10^{2}	$10^{-5}+10^{-4}$
MOLTEN SALTS	$10^{-1}+10^{0}$	$10^{0}+10^{-1}$	10^{1}	10^{-3}	10^{1}	10^{-3}	10^{2}	10^{-4}	10^{2}	$10^{-4}+10^{-2}$
SILICON OILS	$10^{-1}+10^{2}$	10^{-1}	—	—	—	—	3.4×10^{2}	$10^{-6}+10^{-3}$	$10^{1}+10^{5}$	$10^{-4}+10^{-1}$
PURE WATER	1.09	8.8×10^{-2}	1.5×10^{1}	4.6×10^{-3}	1.64×10^{1}	6.4×10^{-4}	—	—	—	—
CONTAMINATED WATER	1.09	5.7×10^{-2}	1.5×10^{1}	4.6×10^{-3}	1.64×10^{1}	6.4×10^{-4}	—	—	—	—
NATURAL WAX	1.80	2.9×10^{-1}	—	—	—	—	2.2×10^{2}	1.9×10^{-4}	4.0×10^{2}	2.1×10^{-1}
MOLTEN GLASS	1.08×10^{4}	5.7	—	—	—	—	1.1×10^{2}	6.0×10^{-8}	1.1×10^{6}	1.7×10^{-3}

Table 5(a). Feasible ranges

	C_1 m_1	C_2 m_1	B_1 β_1	B_2 β_1	M_1	r_2	M_2	r_1	l_1	l_2	V_r
1 I_3	≥ 0	$\ge d_{21}$	≥ 0	$\ge -g_{21}$	1	$\mu \ge 0$	×	×	1	1	V_{m_1}
2 II_3	< 0	$\le \frac{3}{2}d_{21}$	$\ge \frac{m}{3}$	$\ge \frac{m_1}{3}-g$		$d \ge 0$			$\varepsilon^{-\frac{m_1}{3}}$	$l_1\varepsilon^{\frac{d_{21}}{2}}$	$V_{m_1 l_1}$
$2'$ III_3		$\ge \frac{3}{2}d_{21}$		$\ge \frac{m_1}{3}-g_{21}$		$\mu \ge \frac{m_1}{3}$				1	
$2'$ IV_3	≥ 0	$\le d_{21}$	≥ 0	$\ge m_1-g$		$d \ge -\frac{m_1}{2}$			1	$\varepsilon^{-\frac{m_1-d_{21}}{2}}$	
2_2 II_4	$< d$	$< \frac{3}{2}d_{21}+d$	$\ge \frac{m}{3}-\frac{4}{3}d$	$\ge \frac{m_1}{3}-\frac{4}{3}d-g$	×	×	1	$d \le 0$	$l_1\varepsilon^{-\frac{d_{21}}{2}}$	$\varepsilon^{-\frac{m_1-\mu-d_{21}}{3}}$	$V_{m_2 l_2}$
$2'_2$ IV_4	$\ge d$		$\ge -\frac{m}{3}-\frac{2}{3}d$					$d \le -\frac{m_1}{2}$	1		

Table 5(b). Feasible ranges

	C_1 β_1+m_1	C_2 β_1+2m_1	B_1	B_2	M_1 β_1	r_2	M_2 β_1	r_1	I_1	I_2	V_r
4 I_1	≥ 0	$\geq d_{21}$	1	$g_{21}\geq 0$	≤ 0	$\mu\geq 0$			1	1	V_{g1}
3 II_1	<0	$<2d_{21}$		$g\geq 0$	$\leq \frac{m_1}{3}$	$d\geq 0$			$e^{-\frac{\beta_1+m_1}{4}}$	$I_{1}e^{\frac{d_{21}}{2}}$	$V_{g1}I_1^2$
3_2 II_1							$\leq \frac{m_1}{3}-\frac{4}{3}d$	$d\leq 0$			
3' III_1		$\geq 2d_{21}$		$\beta_1+m_1\geq -2g_{21}$	$\leq \frac{m_1}{3}$	$\beta_1+m_1\leq 4\mu$				1	
3'' IV_1	≥ 0	$<d_{21}$		$\beta_1+m_1\leq g$	≤ 0	$\beta_1+m_1\geq -2d$			1	$e^{-\frac{\beta_1+m_1-d_{21}}{2}}$	V_{g1}
$3''_2$ IV_1							$\leq -\frac{m_1}{3}-\frac{2}{3}d$	$\beta_1+m_1\leq -2d$			

Table 5(c). Feasible ranges

	C_1 β_1+m_1	C_2 β_1+m_1	B_1	B_2	M_1 β_1	r_2	M_2 β_1	r_1	I_1	I_2	V_r
6 I_2	$\geq -g_{21}$	$\geq 2d_{21}-g$	$g_{21}\leq 0$	1	$\leq -g_{21}$	$\mu\geq 0$			1	1	V_{g2}
5 II_2	$\leq -g$	$<2d_{21}-g$	$g\leq 0$		$\leq \frac{m_1}{3}-g$	$d\geq 0$			$I_{1}e^{-\frac{d_{21}}{2}}$	$e^{-\frac{\beta_1+m_1+g_{21}-d_{21}}{4}}$	$V_{g2}I_2^2$
5_2 II_2							$\leq \frac{m_1-4d}{3}-g$	$d\leq 0$			
5' IV_2	$\geq -g$		$\beta_1+m_1\geq g$		$\leq m_1-g$	$\beta_1+m_1\geq -4d-g$			1		
$5'_2$ IV_2							$\leq \frac{m_1-4d}{3}-g$	$\beta_1+m_1\leq -4d-g$			
5'' III_2	$<-g_{21}$	$\geq 2d_{21}-g$	$\beta_1+m_1\leq -2g_{21}$		$\leq -\frac{m_1}{3}-g_{21}$	$\beta_1+m_1\leq$ $\leq 2d-g+2d_{21}$			$e^{-\frac{\beta_1+m_1+g_{21}}{2}}$	1	V_{g2}

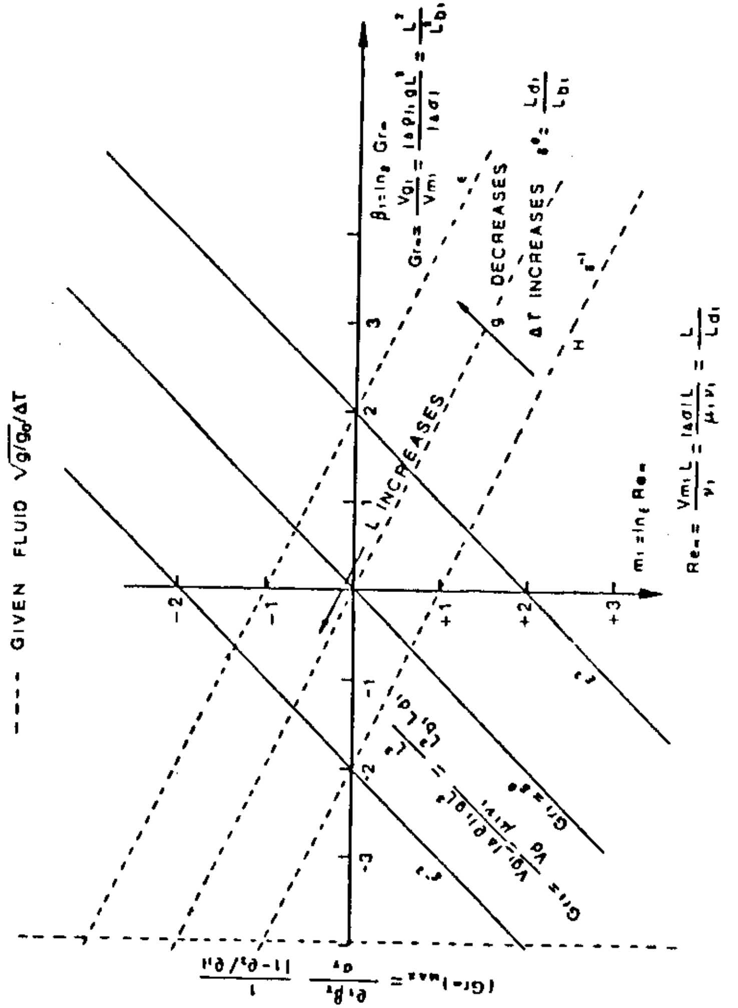


Fig. 1. Properties of β_1, m_1, plane.

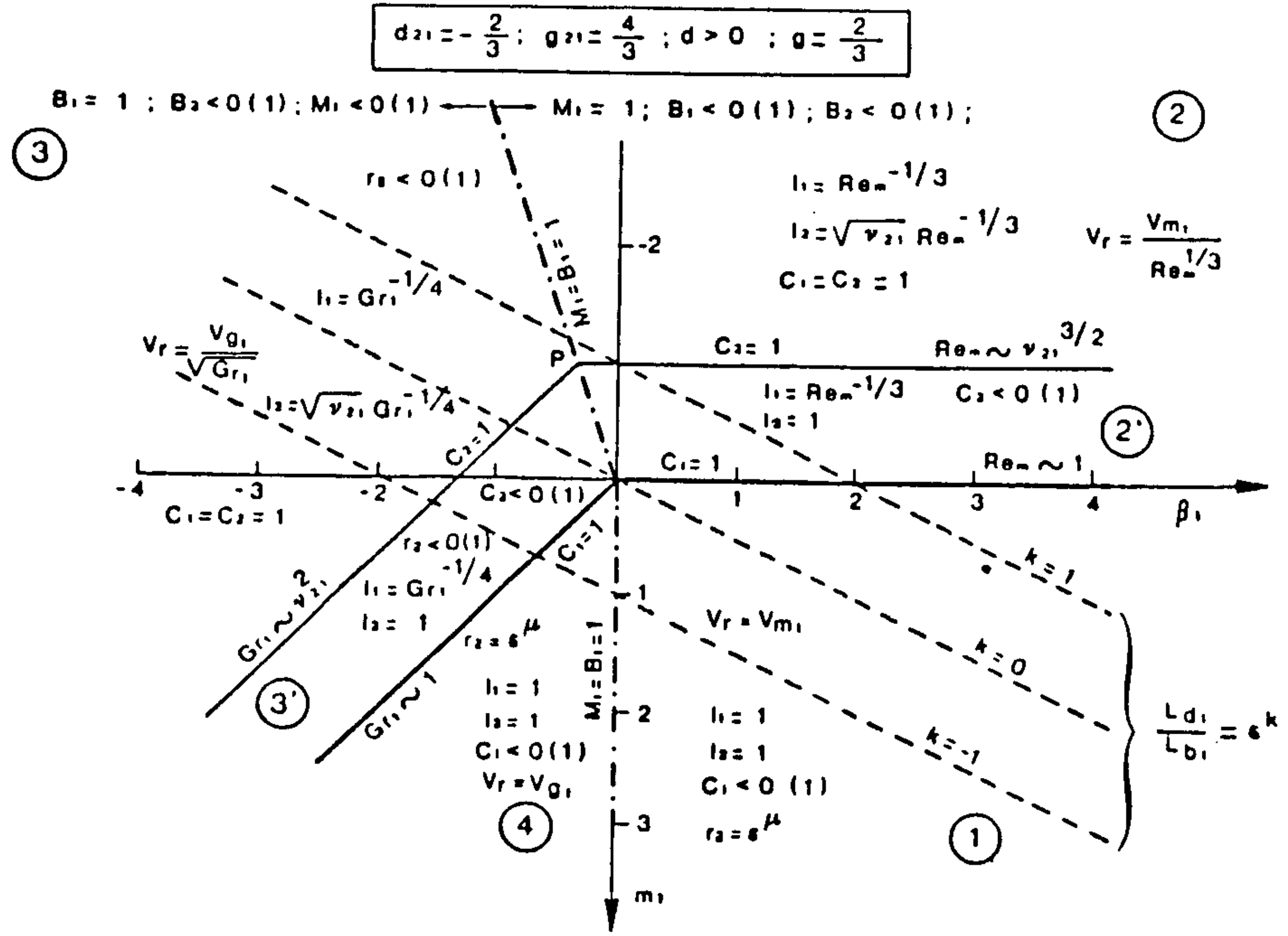


Fig. 2(a). Schematic representation of solutions: case A_1 of Table 1.

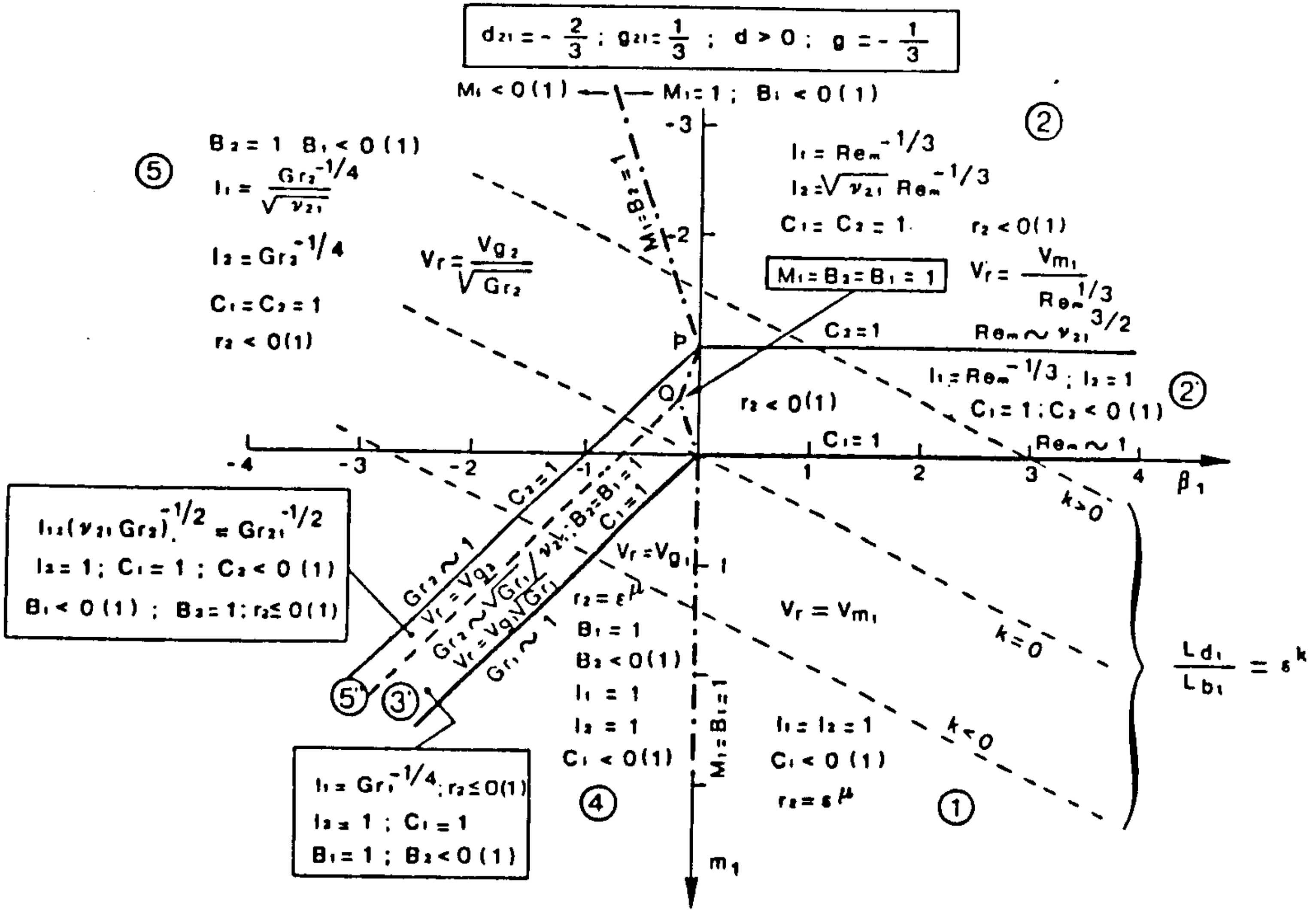


Fig. 2(b). Continued: case A_2 of Table 1.

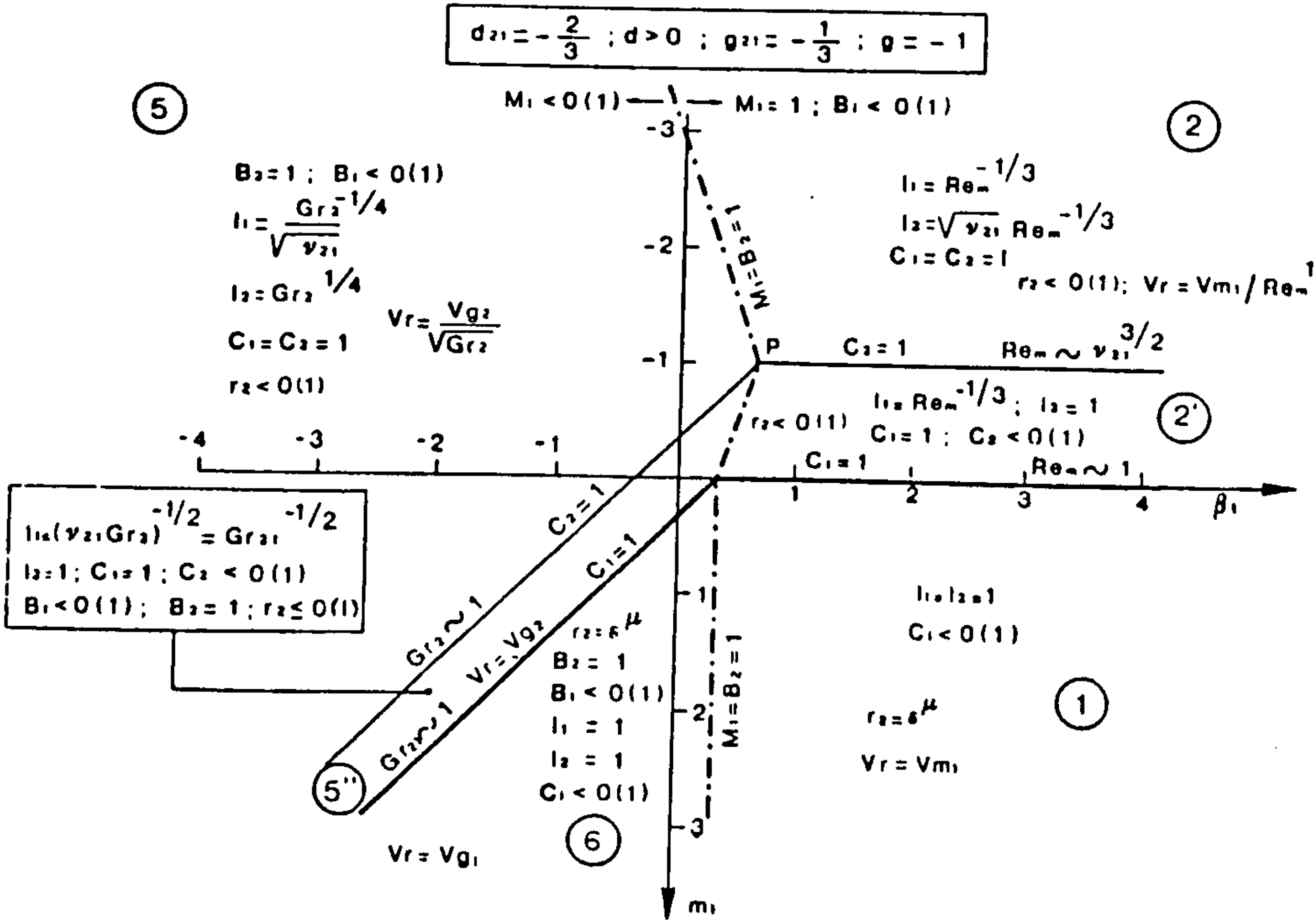


Fig. 2(c). Continued: case A_3 of Table 1.

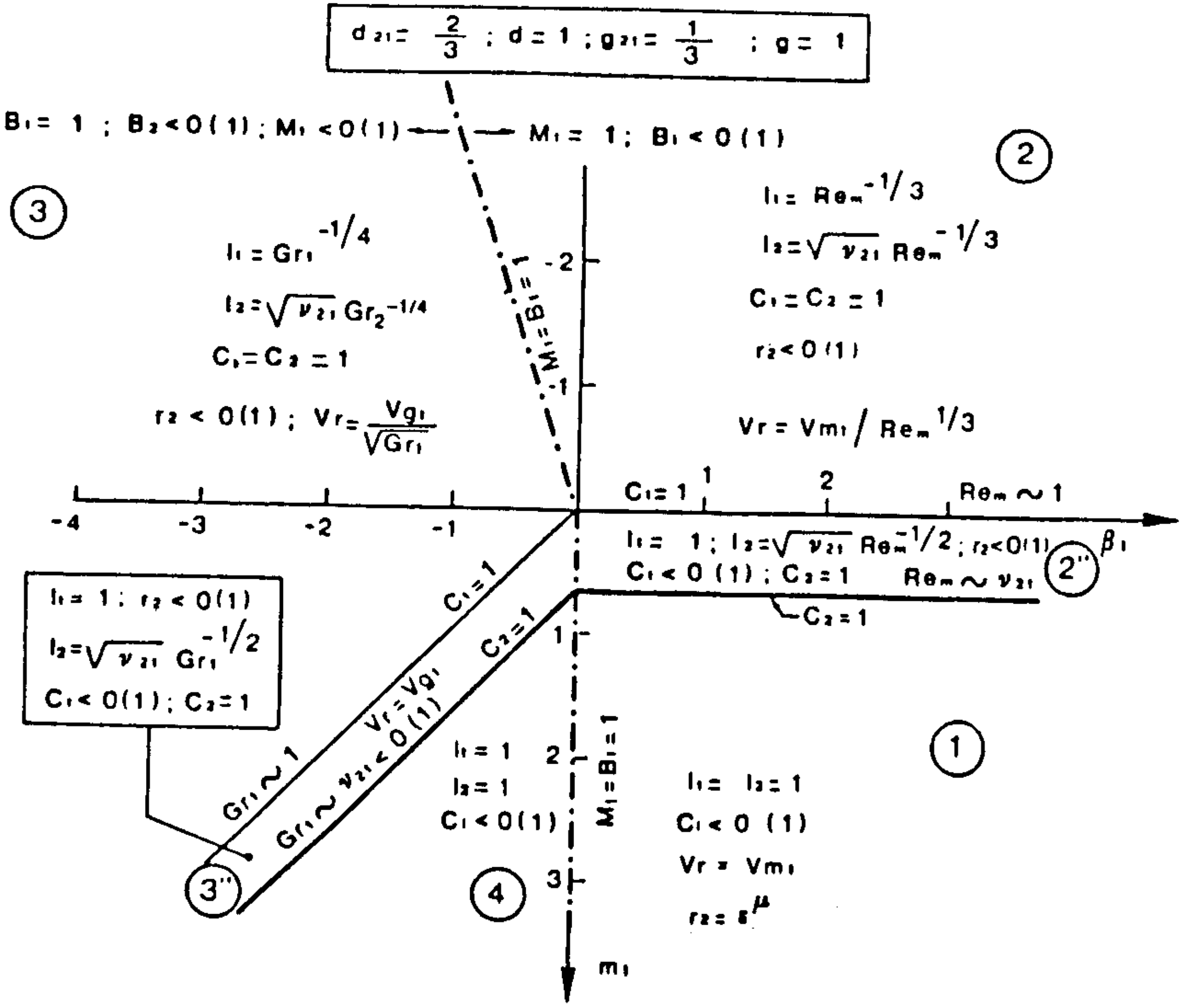


Fig. 2(d). Continued: case B_1 of Table 1.

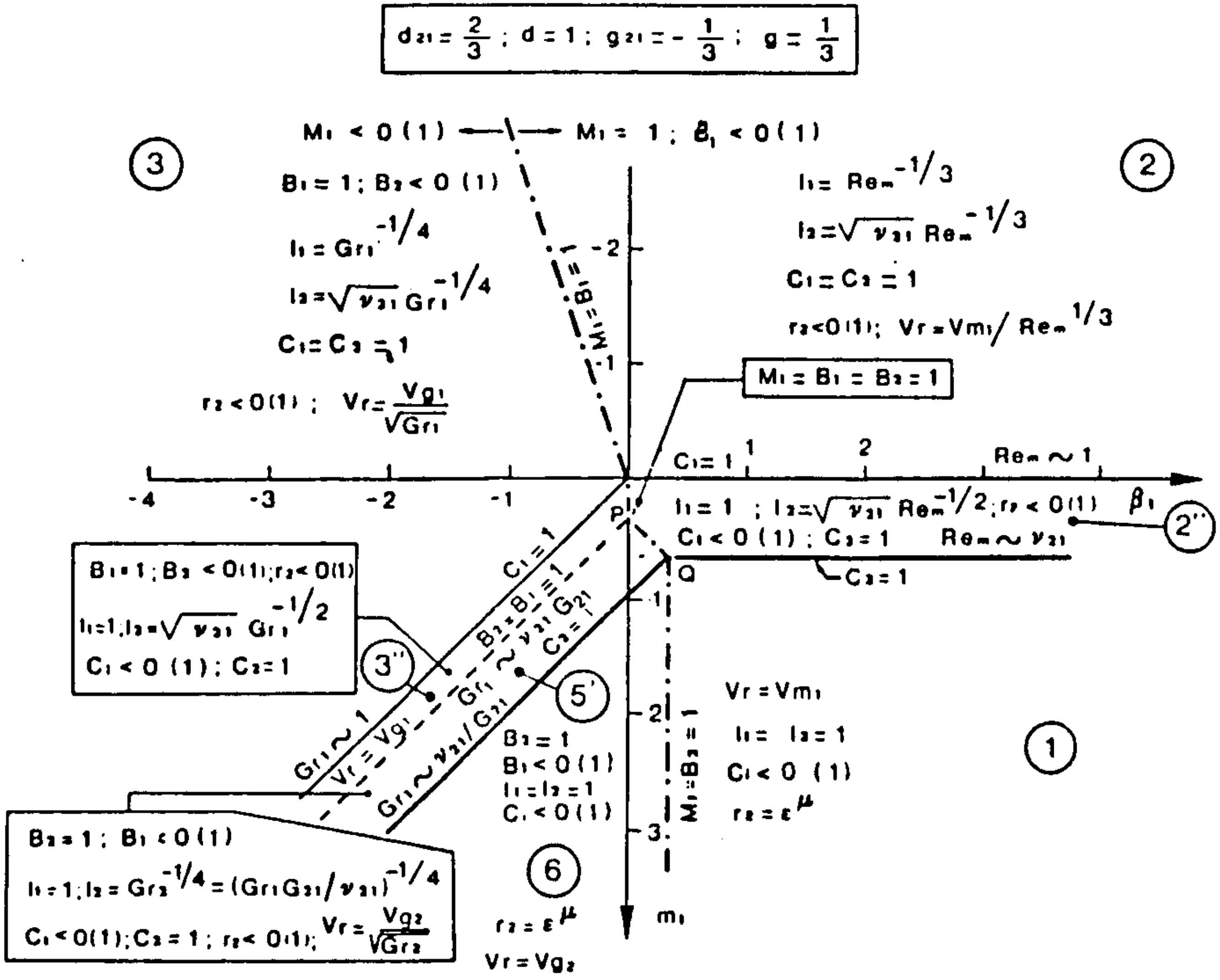


Fig. 2(e). Continued: case B_2 of Table 1.

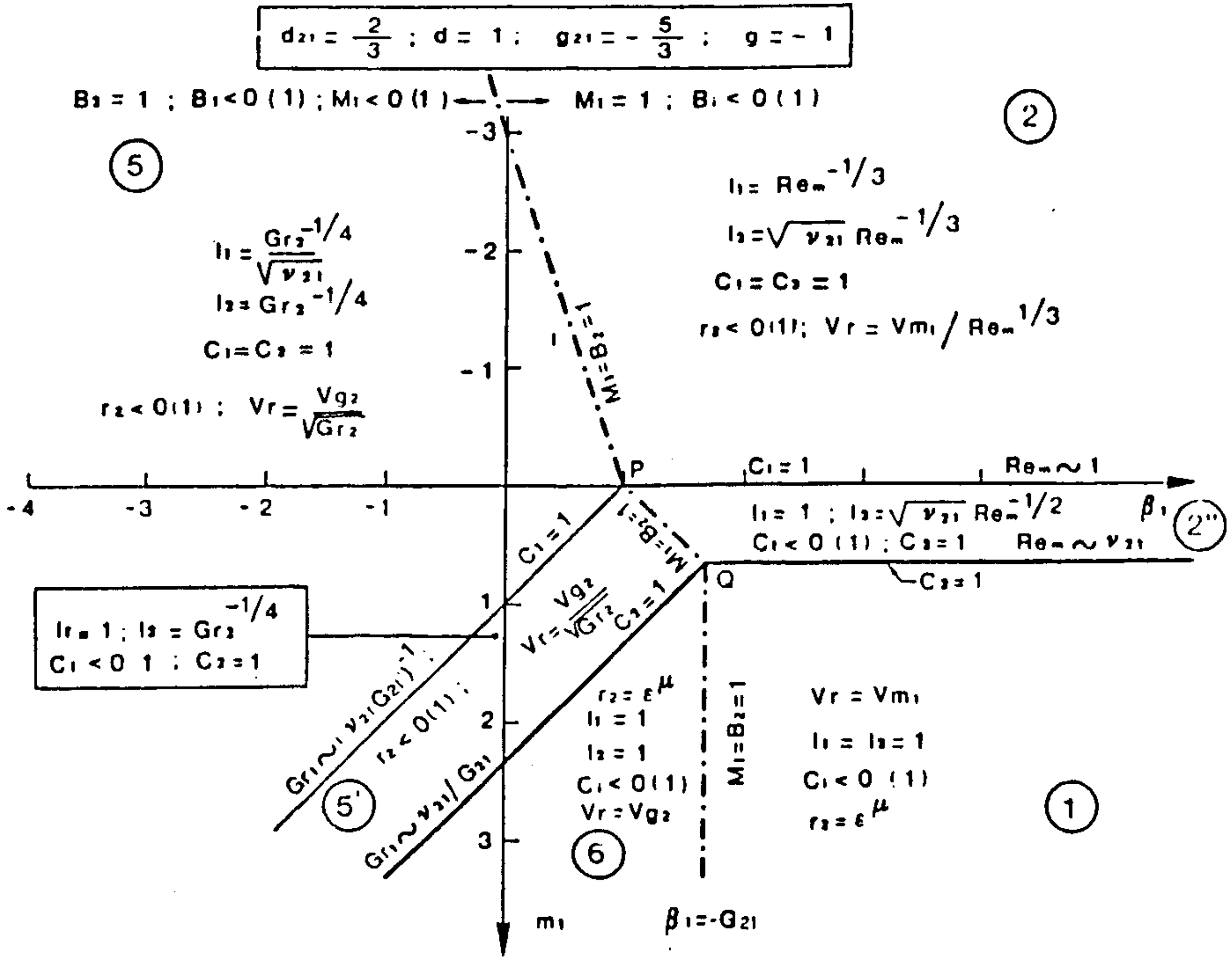


Fig. 2(f). Continued: case B_3 of Table 1.

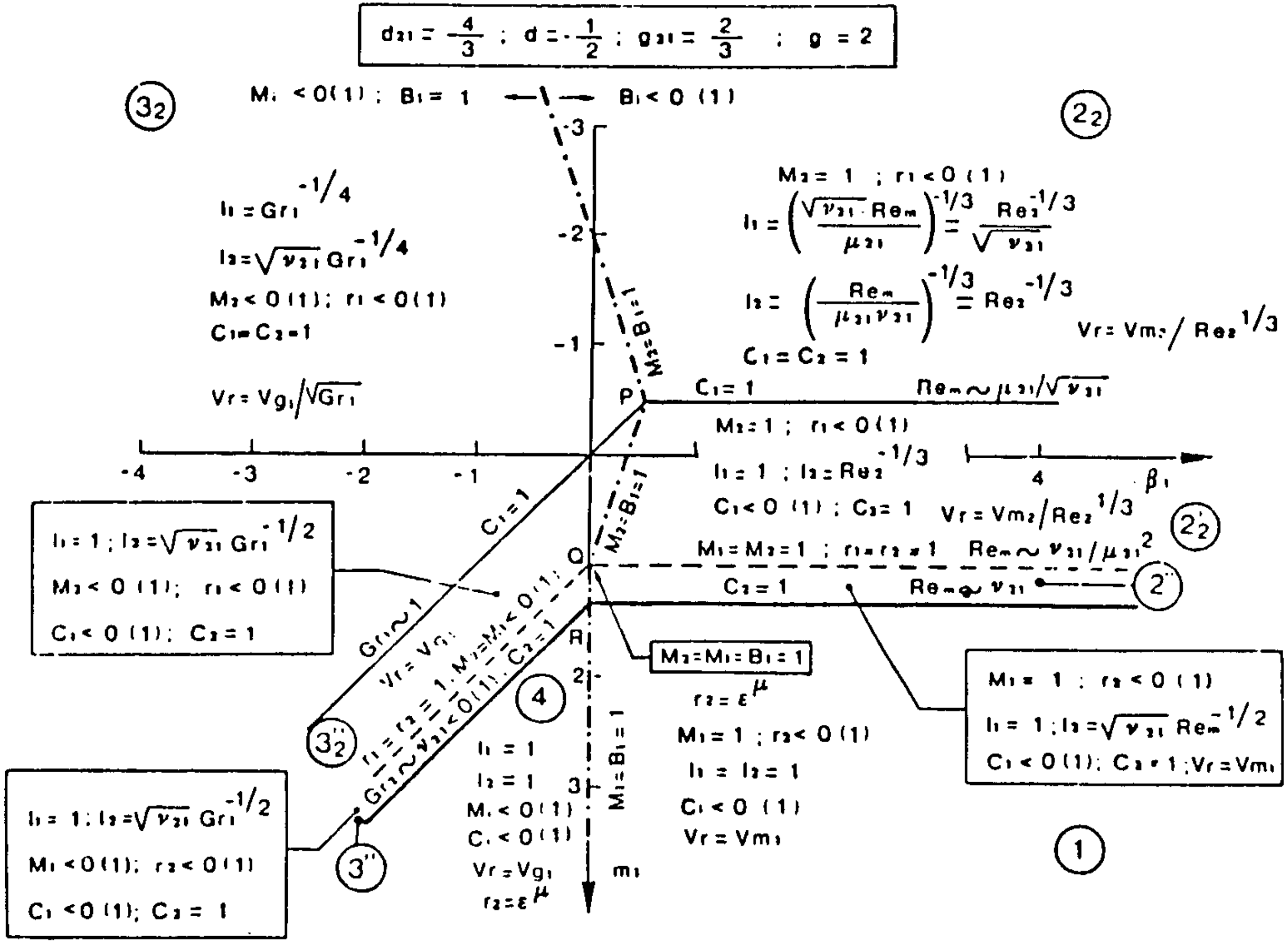


Fig. 2(g). Continued: case C_1 of Table 1.

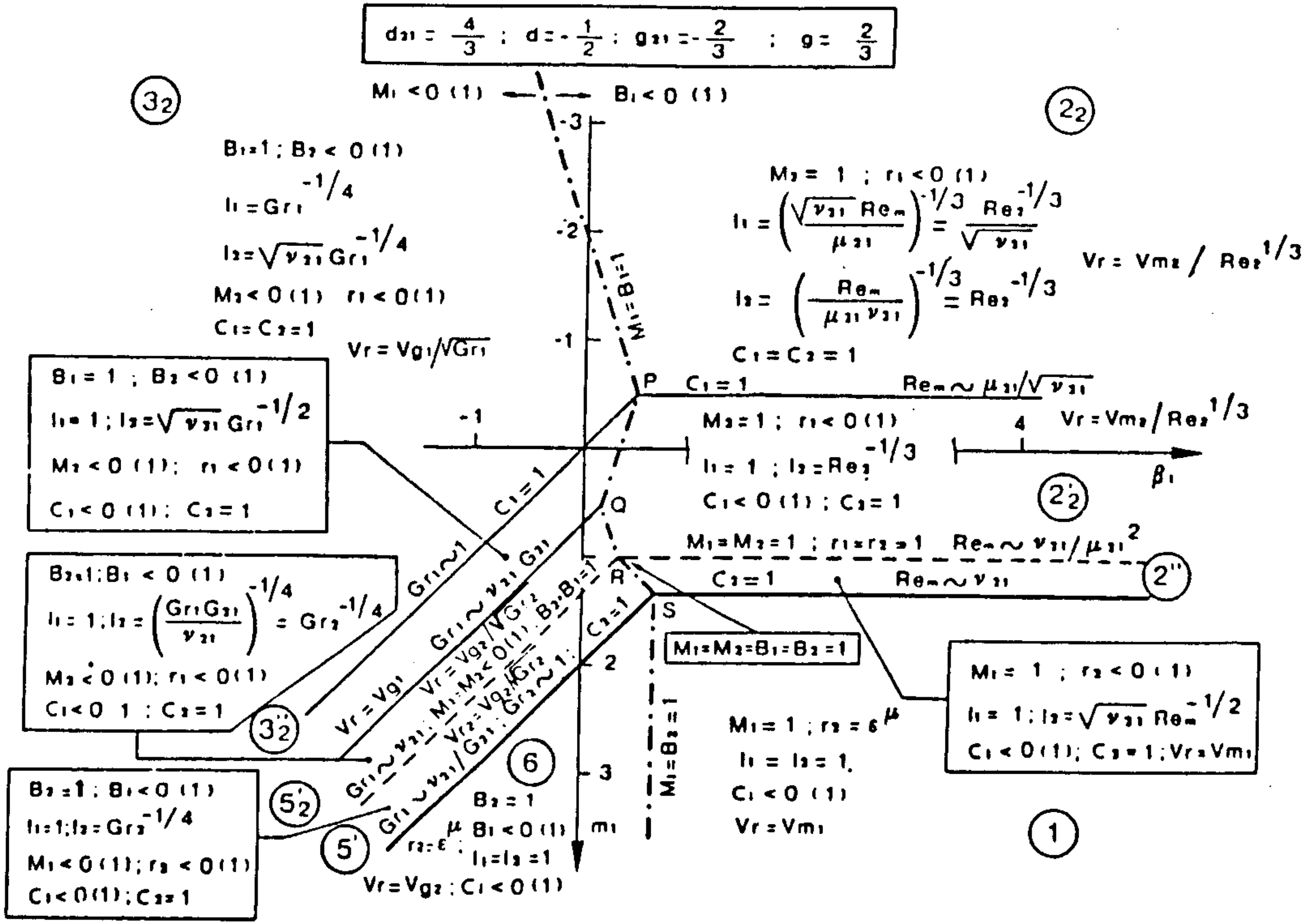


Fig. 2(h). Continued: case C_2 of Table 1.

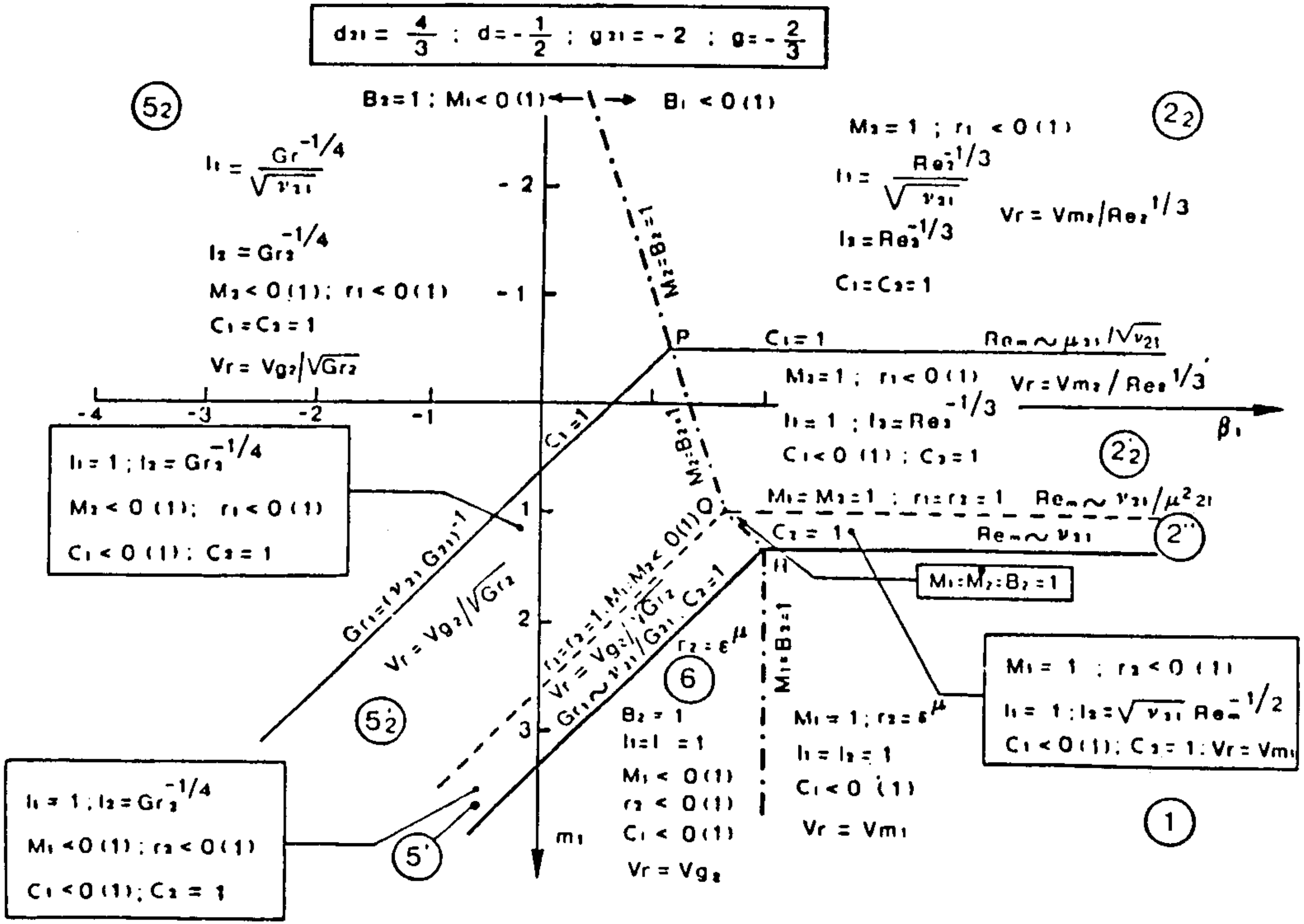


Fig. 2(i). Continued: case C_3 of Table 1.

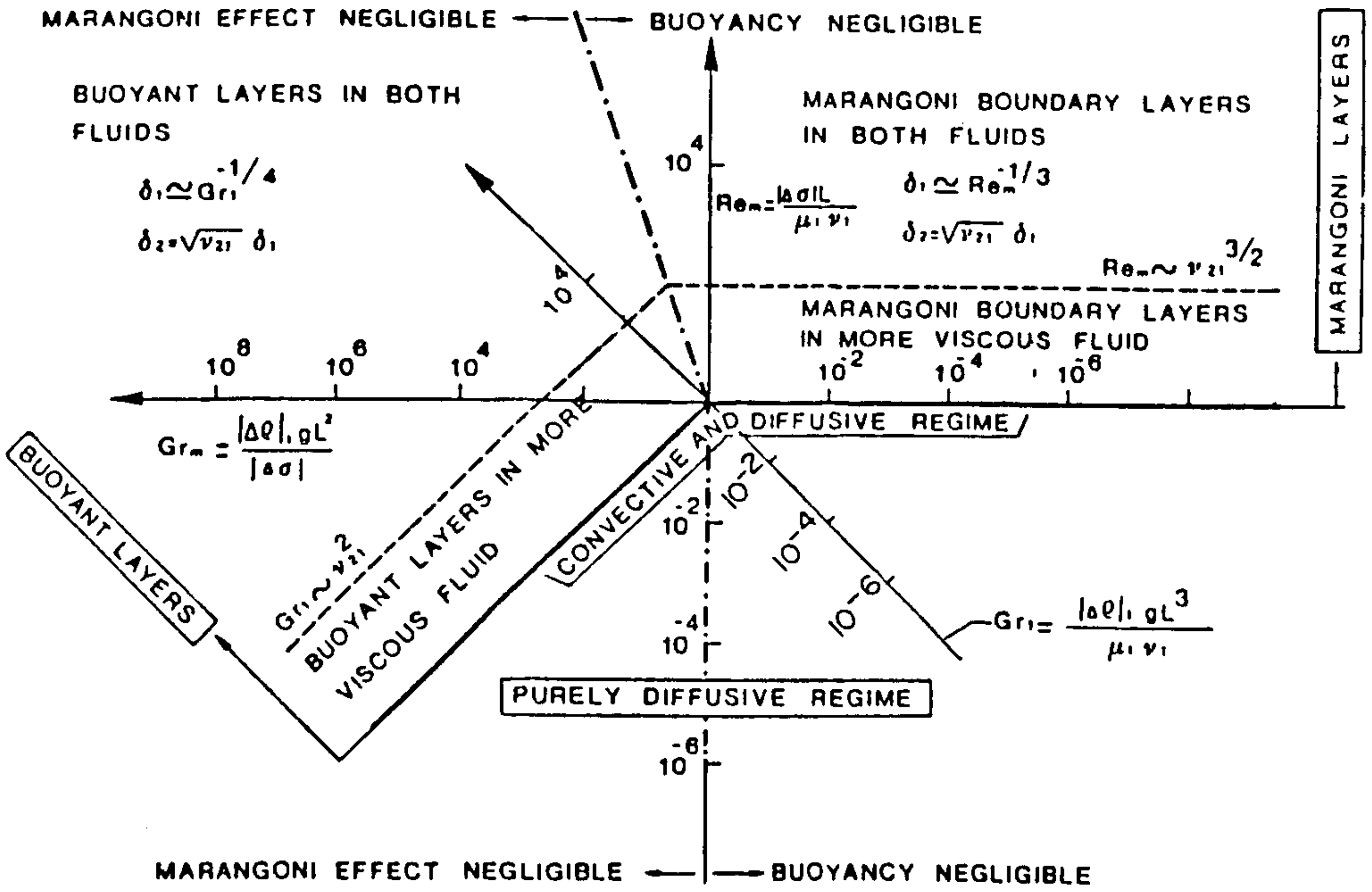


Fig. 3. Summary of free convection regimes for liquid gas system: Re_m, Gr_m plane.

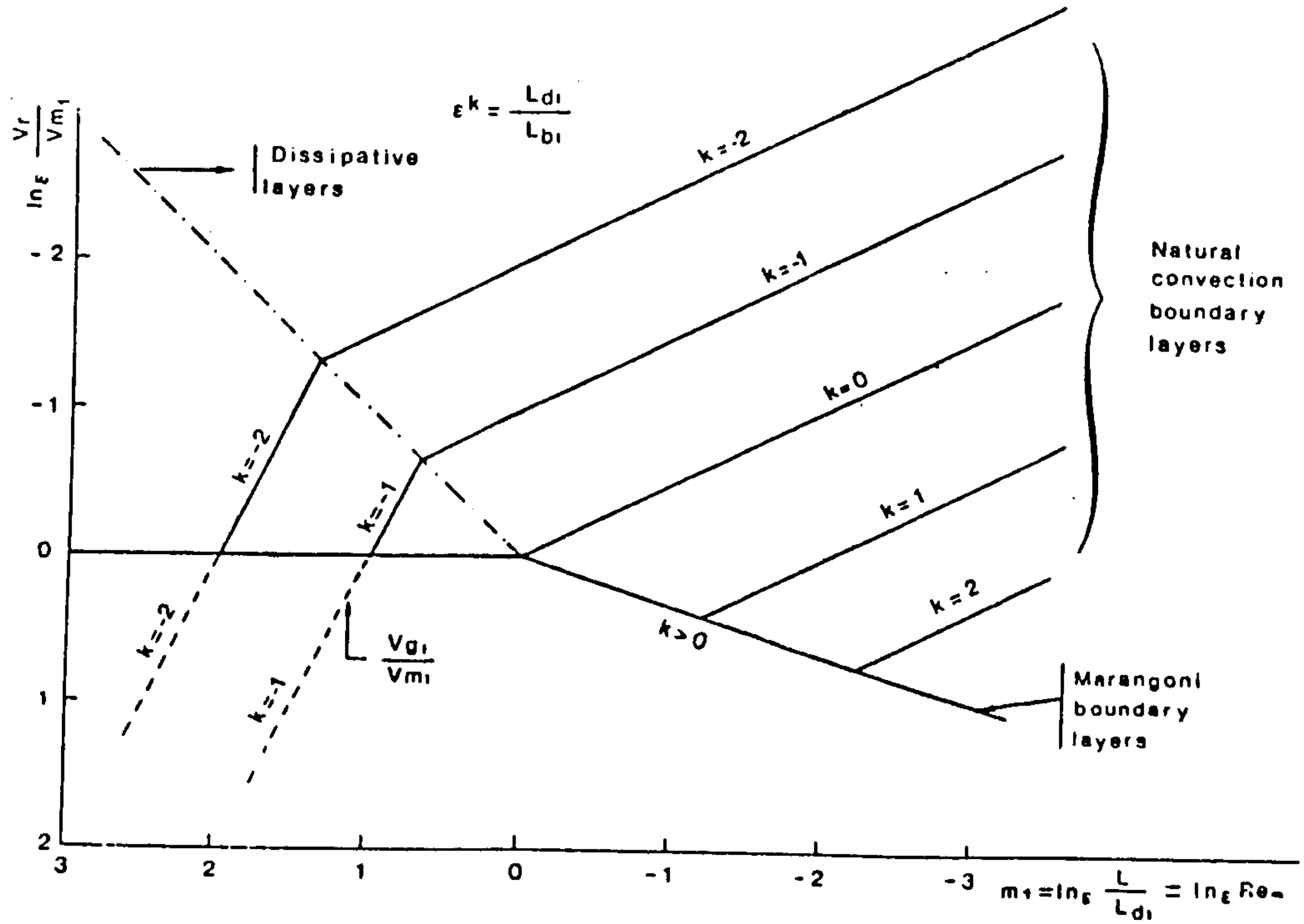


Fig. 4. Reference velocity for liquid-gas systems.

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