MICRO - GRAVITY STUDIES FOR SOLID/LIQUID PHASE CHANGE

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ABSTRACT

Some problems of solid/liquid phase change are presented. Attention is focused on *interface modeling* for numerical analysis, and one-directional growing and melting. Microgravity relevance of some situations is emphasized. Attention is paid to recent activities of the *French Research Group : "Transport Phenomena and Phase Transitions in Microgravity"* GDR-P2TPM (presently GDR-MFA for Fundamental and Applied Microgravity) of Centre National d'Etudes Spatiales (CNES) / Centre National de la Recherche Scientifique (CNRS).

INTRODUCTION

Solid/liquid phase changes are sensitive to gravity. The interfacial zone is often very complex to describe. Indeed, front curvature and solid phase structure depend on several factors and it will be interesting to eliminate some of them due to gravity for a best understanding of solidification and melting processes.

Experiments in microgravity conditions are necessary, in drop towers, parabolic flight, sounding rockets and satellites. An experimental facility, named **DECLIC**, will take place in the **ISS**. *Experiments on transparent material solidification will be performed in DECLIC*.

It is very useful to perform calculations with and without gravity effects and to compare with experimental results.

Teams working on these topics in the French Research Group : "Transport Phenomena and phase transitions in Microgravity" (GDR - P2TPM and MFA - CNES/CNRS)

- Solidification from the melt (*Bernard Billia*, Laboratoire Matériaux et Microélectonique de Provence Marseille)

- Solidification fronts (Gabriel Faivre, Groupe de Physique des Solides Paris)

- Instabilities, crystal growth and microgravity (*Daniel Henry, Hamda Benhadid*, Laboratoire de Mécanique des Fluides et d'Acoustique de Lyon)

- Elasticity and growing (*Alain Pocheau*, Institut de Recherche sur les Phénomènes Hors d'Equilibre)

-Influence of external fields on solidification (*Thierry Duffar, René Moreau*, Elaboration par Procédés Magnétiques Grenoble)

-Numerical modeling (*Patrick Bontoux, Pierre Haldenwang, Mohammed El Ganaoui*⁽¹⁾, Laboratoire de Modélisation et Simulation Numérique en Mécanique Marseille, ⁽¹⁾ Université de Limoges)

-Thermal, thermosolutal and thermovibrational convection in microgravity (*Abdelkader Mojtabi*, Institut de Mécanique des Fluides de Toulouse)

-High performance calculations in microgravity/ vibrationnal convection (*Bernard Roux*, Laboratoire de Modélisation et Simulation Numérique en Mécanique Marseille)

BASIC CONSIDERATIONS

Natural convection

Microgravity is relevant for fluid flows when density gradients are large and forced convection not too important.

Grashov number

$$Gr = \Delta \rho g L^3 / v^2$$

$$\Delta \rho = \rho - \rho_{\infty}$$

$$\rho_{\infty}$$

$$\nu = \mu / \rho$$

$$L$$

local density deviation

corresponds to the liquid at rest at the same altitude kinematical viscosity,

characteristic length

Reynolds number Re=UL/v

(U characteristic velocity : if U is the

buoyancy characteristic velocity, then

$$Re=\sqrt{Gr}$$
)

Rayleigh number

$$\frac{Ra_{T}}{Ra_{T}} = Gr_{T}Pr = g\beta_{T}\Delta TL^{3}/v\lambda , \quad \frac{Ra_{C}}{Ra_{C}} = Gr_{C}Sc = g\beta_{C}\Delta CL^{3}/vD$$

subscripts (,) and (,) refer to thermal and solutal origin of $~\Delta\rho~$:

$$\Delta \rho = \beta_T \Delta T , \qquad \Delta \rho = \beta_C \Delta C$$

Marangoni number

$$Ma_{T} = (\partial \sigma / \partial T) (\partial T / \partial x) L^{2} / \mu \lambda \quad , \quad Ma_{T} = (\partial \sigma / \partial C) (\partial C / \partial x) L^{2} / \mu D$$

The *classical Rayleigh-Bénard thermal instability* occurs in a fluid layer heated from below.

Solidification process is generally more complex

In directional solidification of alloys inside a cylindrical vertical crucible, the solidification layer is moving and the *solidification front in not planar*, upward temperature gradient is generally positive, there is a coupling between temperature and concentrations. Radial thermal gradients drive natural convection and modify concentration fields

Marangoni effect and Marangoni instability

They can occur in *floating zone* solidification (or in other solidification procedure, when the *contact between the fluid phase and the wall* of the crucible is not ensured, as it is often the case in microgravity), where there is a *liquid-gas or liquid-liquid* (monotectic alloys) interface.

Instabilities and coupling

On the ground, the *Marangoni effect* is coupled with *Rayleigh-Bénard instability*. Marangoni-Bénard instability can be coupled to *Soret effect*, possibly in microgravity.

Magnetic field is used for measuring diffusion coefficients in liquids, or for compensating for gravity, and numerical studies have been performed about coupling between buoyancy and magnetic effects.

MORPHOLOGICAL INSTABILITIES IN DIRECTIONAL SOLIDIFICATION

"Convection effects strongly influence the development of solidification microstructures. However, most microstructure models are based on purely diffusive transport mechanisms. For this reason, crucial benchmark data required to test fundamental theories of microstructural pattern formation have resulted from solidification experiments conducted in *microgravity environment*, where convection effects can be substantially reduced, and/or from ground based experiments with restricted samples sizes where convection effects can be eliminated" (Karma, A. (2001) *Microstructural patern formation during solidification*, Introduction à la session 2 (Solidification et croissance cristalline) du Colloque « Sciences de la matière et microgravité », 14-15 mai, ESPCI, Paris.)

Complex phenomena are observed in real systems such as

- **1.** curvature of the front in relation to convective instabilities
- **2. eutectic colony formation** (which have been observed in thinsample directional solidification of the transparent eutectic alloy CBr₄-C₂Cl₆. *Fig. 1* shows *existence of colonies when impurities are present.*)



Fig. 1: Eutectic colonies in CBr4-C2Cl6-Naphtalene, $V = 31 \mu m s-1$ (Akamatsu, S.; Faivre, G. 2000 Physical Review E 61, 3757-3769.)

The transition between planar lamellar eutectic front and eutectic colonies goes through intermediate structures as traveling waves (*Fig. 2*) and two-phase fingers (*Fig. 4*) which has been recently observed and are now studied by linearized theory or by phase field method.



Fig. 2: Traveling waves under the threshold of colony formation V = 13.5 μ m s⁻¹. (Akamatsu, S.; Faivre, G. 2000 Physical Review E 61, 3757-3769.)



Fig. 3 Lamellar branching during lateral invasion (towards the right) of a front a by the phase b (Akamatsu, S.; Moulinet, S.; Faivre, G. 2001 *Metall. Mater. Trans.* **32A**, 2039-2048.)



Fig. 4: Two-phase fingers a-b-a. V = 4.1 μ m s-1. (Akamatsu, S.; Faivre, G. 2000 Physical Review E 61, 3757-3769.)

MELTING AND THERMAL STABILIZATION

-Dynamics of melting (preparatory to directional solidification) : criterion for morphological instability in directional melting (melting is not the mere reversal of free crystal growth) interest of experiments in the limit of diffusive transport of solute in the liquid, that *imposes to work* in the absence of gravity **DECLIC** -Two phenomena have been observed in situ and in real time during directional melting of transparent succinonitrile-acetone alloys in a cylinder: 1)nucleation and growth of liquid droplets in the bulk solid and 2) liquid dendrites, due to morphological instability of the phase -boundary.



Fig. 5: a) Liquid droplets inside grains; b), c) Morphological instability at grain
Boundaries; d) Arrays of melting dendrites in a grain (Benielli, D., Bergeon, N., Jamgotchian, H., Billia, B. & Voge, Ph. 2002, Phys. Rev. E, 65, 051604)

INTERFACIAL MODELING AND APPLICATIONS *Transition-zone*

Interfacial zone is often very complex to study.

A critical problem for numerical resolution is the presence of an interfacial discontinuity at the boundary between phases. To avoid this difficulty, some authors have replaced the discontinuity by a continuous description of the transition region. This is the concept of phase field.

There are two classes of phase field method, which differ by the scale of the description: macroscopic, and microscopic - or mesoscopic.

A mushy zone description

The macroscopic method is applied to *dendritic-like porous structures*.

A Darcy source term

$$\frac{2}{(\vec{v}-\vec{v}_s)}$$
 appears on the right-hand side of momentum

equation where K denotes the isotropic permeability and represents the direct link between microscopic morphology and the macroscopic equations of conservation.



a. Digitized image from a dendritic structure of Succinonitrile-acetone



b. Macroscopic dendritic mushy zone and an associated averaging volume

Fig. 6. The mushy zone (Goyeau B., Benihaddadene T., Gobin D. & Quintard M. 1999, Metall. Mat. Trans., 30B, 613)

Morphological instability in directional melting and thermal stabilization

The criterion for morphological instability in directional melting becomes:

$$V > V_{MI} = (kD_{S} + D_{L})G/[mC_{0}(k-1)] \cong D_{L}G/[mC_{0}(k-1)]$$

 V_{MI} : critical melting velocity, C_0 : initial solute concentration, D_s, D_L diffusion coefficients

Dendritic orientations/liquid-solid interface is determined by the anisotropy of solid succinonitrile that favors growth in <100>direction and grain orientation. The formula may be applied with C_{loc} instead of C_0 .

Droplet growing in the superheated solid during directional melting

Parameters

The length $L_{_{SH}}$ of the superheated solid

$$L_{SH} = mC_0 (k-1)/Gk$$

The global droplet velocity is the difference $V_{\mu}=V_{\mu}-V_{\mu}$ between the pulling

velocity and the migration velocity

$$V_{mig} = -GD_L / [mC_L (k-1)]$$

Mechanism of migration of the liquid droplets: by TGZM (Temperature Gradient Zone Melting)

Modeling of the growth of the droplets

General equation:

$$\frac{\partial^2 C_0(r,0)}{\partial r^2} + \frac{1}{r} \frac{\partial C_0(r,0)}{\partial r} = 0$$

At the droplet solid/liquid interface:

$$\left[C_{L}(T) - C_{S}(T)\right]V_{R} = D_{S} \frac{\partial C(r,0)}{\partial r}\Big|_{R}$$

 V_{R} is the growing velocity and T verifies:

$$T = T_0 - G(Z - Z_0) + GV_P(t - t_0)$$

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Fig. 7: Sketch of the TGZM process. The concentration gradient resulting from the temperature gradient induces solid diffusion inside the droplet that in turn causes melting at the droplet hot end (top) and solidification at the cold end (bottom) (Benielli, D. et al. Ph. 2002, Phys. Rev. E, 65, 051604)

during

Calculation of the droplet concentration $\rho(X,t)$ directional melting and thermal stabilization

 $\frac{\partial \rho}{\partial t} + \frac{\partial \left(\rho V_{mig}\right)}{\partial X} = 0$

During the melting phase $t \le t_0$, a moving boundary condition $\rho(X_B,t)$ is used at the altitude X_B where $T(X_B,t)=T_E$.

Stopping the furnace at time t_0 , the temperature remaining constant during the stabilization, the boundary becomes $\rho(0,t) \approx 0$



Fig. 8. Profiles giving both the number-density and solute concentration calculated from our model for Al–1.5 wt% Ni alloys. Continuous lines are calculated with $G_d = G_s$; from top to bottom: $t = t_0 = 1250$ s (complete melting), $t_1 = t_0 + 1$ h, $t_2 = t_0 + 3$ h, $t_3 = t_0 + 5$ h, $t_4 = t_0 + 7$ h. Dashed line is calculated with $G_d = G_L$ and for $t_1 = t_0 + 1$ h.

Enthalpy method

Benielli et al., El Ganaoui and Guérin et al. consider a single set of homogenous balance equations adapted to the problem of phase change in a 2D configuration.

In this method they introduce an average density ρ weighted by the liquid and solid mass fractions, \vec{v} , \vec{v}_s , C and h are *averaged local quantities* weighted by the liquid and solid volume fractions. For instance one has:



With this model, including appropriate closure relations and boundary and initial conditions, it is possible to obtain isotherms and streamlines which show, in particular, the position of a curved smooth interface (*Fig. 9*).

Interfacial modeling

French micro-gravity studies for solid/liquid phase change *R. Prud'homme LMM CNRS/UPMC Paris*



Fig. 9: Isotherm and streamline plots obtained with SNC for pulling velocity $V_t=10\mu ms^{-1}$, and thermal gradient G \cong 30K/cm Interface position around y=0.75, corresponds to the gray line [Benielli, D., El Ganaoui, M., Semma, E., Bergeon, N., Jamgotchian, H., Voge, P., Billia, B. & Bontoux, P. (2001) *J. Phys. IV France*, **11**, Pr6-135-142.]

Phase field model for microstructures

To explain microstructures in constrained growth, and recently in eutectic colony formation, Plapp and Karma have studied the problem first analytically and then numerically, using a phase field model. They introduce a phase field $\phi(x,z,t)$ that distinguishes between solid and liquid. They study a ternary alloy close to a binary eutectic which, for simplicity, they assume to have a symmetric phase diagram. They introduce a phase field. They start from a dimensionless Helmholtz free energy functional

$$F = \int_{V} \left[\frac{W_{u}^{2}}{2} (\vec{\nabla} u)^{2} + \frac{W_{\phi}^{2}}{2} (\vec{\nabla} \phi)^{2} + f(\phi, u, \vec{c}, T) \right] dV$$

$$f(\phi, u, \vec{c}, T) = \frac{\phi^{2}}{4} + \frac{\phi^{4}}{8} + \frac{1 + h(\phi)}{2} f_{sol}(u, \vec{c}, T) + \frac{1 - h(\phi)}{2} f_{liq}(u, \vec{c}, T)$$

u is a scaled concentration , C_E , C_{α} and C_{β} are the compositions of the liquid and the two solid phases in the pure binary eutectic at the eutectic temperature T_F

 $u(x,z,t) = \frac{C(x,z,t) - C_E}{(C_B - C_a)/2}$, $\tilde{C}(x,z,t)$ concentration of impurities,





 $f_{sol}(u, \tilde{C}, T)$, $f_{liq}(u, \tilde{C}, T)$

h(ϕ)= $\frac{3}{2}\left(\phi - \frac{\phi^3}{3}\right)$

free energy densities for solid and liquid, respectively,

 w_u , $w_{\!\varphi}$ characteristic thicknesses of the solid-solid and of the solid-liquid interface, respectively,

 $M(\phi,u,\widetilde{C})$, $\widetilde{M}(\phi,u,\widetilde{C})$ mobility functions of the eutectic component and the ternary eutectic, respectively

They deduce, three local equations between three variables, which are valid everywhere under appropriate assumptions

 $\tau \frac{\partial \phi}{\partial t} = W_{\phi} \vec{\nabla}^2 \phi + \frac{\phi}{2} - \frac{\phi^3}{2} + h'(\phi) \left(f_{lia} - f_{sol} \right)$

$$\frac{\partial \mathbf{u}}{\partial t} = \vec{\nabla} \cdot \left[\mathbf{M} \left(\frac{\partial^2 \mathbf{f}_{liq}}{\partial u^2} \vec{\nabla} \mathbf{u} + \mathbf{W}_u^2 \vec{\nabla} \left(\vec{\nabla}^2 \mathbf{u} \right) \right) \right]$$

$$\frac{\partial \widetilde{C}}{\partial t} = \vec{\nabla} \cdot \left(\widetilde{M} \frac{\partial^2 f_{liq}}{\partial \widetilde{C}^2} \vec{\nabla} \widetilde{C} \right)$$

2D phase-field simulations: eutectic formation



Expriment (S. Akamatsu, G. Faivre 2000, Phys. Rev. E, 61, 3357)



Simulation - "phase field" method (*R. Folch, M. Plapp, 2001*)

Fig. 10: Lamellar eutectics

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The authors found a good overall agreement with their theoretical predictions of linear analysis, which predicts a destabilization front by long-wavelength modes that may be stationary or oscillatory. But *they find that the growth of the lamellae is not exactly normal to the large scale envelope of the composite interface*, a rule used in the linear stability analysis.

The phase field model must be extended to 2D interfaces in 3D configuration (*Fig. 12*).

The authors (S. Akamatsu *et al.*) propose to compare benchmark space experiments to ground ones, and also to study the intermediate case of semi-massive samples.

3D phase-field simulations: stability of hexagonal solidification paterns



- $l_{_D}$: diffusion length
 - : thermal length

$$\nu = l_T / l_D$$

- *a,b* : distance between rods in x and y
- \mathcal{E}_{4} : capillary anisotropy

Fig. 12: Triplets at v = 12.5, $a/l_{D} = 5.333$ $b/l_{D} = 4.640$, and $\varepsilon_{4} = 0.02$. Six cells were simulated and the final picture was replicated four times to yield a clearer view (Plapp, M., Dejmek, M.2004, *Europhysics Lett.* **65**, 2 p. 276-282).

OTHER RELEVANT PROBLEMS

- Self organized dynamics on a curved growth interface



Fig. 13 : Snapshots of the cellular solidification front. Image width is 2.2 mm and V= $1.6 \ \mu ms^{-1}$ Solid phase is bellow the interface. a) On the left side, large cells are displayed as a result of the stretch produced by the tangencial flow driven by interface curvature. These cells are ready to split. b) A few minits later, this cells start to split. (Bottin-Rousseau, S., Pocheau, A. 2001, Phys. Rev. Letters, 87, 076101)

 Crystalline nucleation and phase selection in refractory metals and alloys interest of *microgravity and ultra-vacuum* to ensure absolute no-contact conditions and purification by evaporation of really spherical droplets *drop-tube of CEA* - Solidification front curvature: very important problem experiments will be performed on transparent material for a better knowledge of this phenomena DECLIC instrument

- Control by vibration: studied for stabilizing solidification fronts and obtaining planar fronts reduced gravity experiments are to be performed in this field, for a better understanding of the effects of vibrating fields on fluids, interfaces and multiphase flows

- Gravity level: even in microgravity conditions, solidification remains sensitive to the gravity level and orientation