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In Memoriam Adelina Georgescu

ON THE NONLINEAR STABILITY OF A BINARY MIXTURE WITH CHEMICAL SURFACE REACTIONS[*]

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Abstract

In this work we consider the non linear stability of a chemical equilibrium of a thermally conducting two component reactive viscous mixture which is situated in a horizontal layer heated from below and experiencing a catalyzed chemical reaction at the bottom plate. The evolution equation for the perturbation energy is deduced with an approach which generalizes the Joseph's parametric differentiation method. Moreover, the nonlinear stability bound for the chemical equilibrium of the fluid mixture is derived in terms of thermal and concentrational non dimensional numbers.

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1 Introduction

The convective instability and the nonlinear stability of a chemically inert fluid in a gravitational field heated from below (the classical Bénard problem)

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have been studied and present a well known interesting problem in several fields of fluid mechanics. More recently, [1]-[4] have considered reactive fluids of technological interest for whose chemical reactions can give temperature and concentration gradients which influence the transport process, for example, the dissociation of nitrogen, oxygen or hydrogen gas near the gas-solid interface of a space vehicle when returning to the earth's atmosphere, (see Bdzil and Frisch [1], [2] and Loper and Roberts [5],) and can alter hydrodynamic stabilities.

In the present paper, begun in 2009 when the first Author was still alive and then finished by the second author also developing some A. Georgescu's ideas and suggestions, we consider a fluid mixture composed of the dimer A_2 and the monomer A in a horizontal layer heated from below, the bottom plate being catalytic. We evaluate the effects of heterogeneous surface catalyzed reactions on the hidrodynamic stability of the chemical equilibrium.

The model adopted is that of Bdzil and Frisch.

We consider a Newtonian fluid model and derive the evolution equation for the perturbation energy with the approach from [6], [7],[8], which generalizes the Joseph's parametric differentiation method reported in [9], [10].

A non linear stability bound is derived in terms of all involved physical parameters.

2 The initial/boundary value problem for perturbation

We consider the mixture (A_2, A) described by a Newtonian model to which we apply the Boussinesq approximation in the layer bounded by the surfaces $z = 0$ and $z = 1$ with the lower surface being catalytic, that is, the interconversion $(A_2 \rightleftharpoons A)$ occurs via the surface $z = 0$. However, the conditions that must be satisfied at the catalyzed boundary $z = 0$, are [3]:

$$\vec{J} \cdot \vec{k} = 0 \qquad \vec{Q} \cdot \vec{k} = 0$$

where $\vec{J}$ is the mass flux, $\vec{k}$ is the unit vector in the vertical upward direction, and Q is the heat flux. The chemical equilibrium S_0 is characterized by the following temperature $(\overline{T})$ and degree of dissociation (fraction of pure monomers present) $(\overline{C})$ fields [2], [3]:

$$\overline{T}(z) = T_1 + \beta(1 - z), \qquad \overline{C}(z) = C_1 + \gamma(1 - z), \tag{1}$$

where C_1 and T_1 are the values of C and T at $z = 1$ and the constants β and γ are given in [1], [3].

Let us now perturb S_0 up to a cellular motion (convection-diffusion) characterized by a velocity $\vec{u} = \vec{0} + \vec{u}$, a pressure $p = \bar{P} + p'$ a temperature $T = \bar{T} + \theta$ and a concentration $C = \bar{C} + \gamma$ fields, where $\vec{u}, p', \theta, \gamma$ are the corresponding perturbation fields and $\vec{0}, \bar{P}, \bar{T}, \bar{C}$ represent the basic state S_0 (the expression of $\bar{P}$ follows from the momentum equation for S_0). The perturbation fields satisfy the following equations which express the conservation of the momentum, energy and concentration, written in nondimensional coordinates [4], [11]

$$\frac{\partial}{\partial t}\vec{u} + (\vec{u}\cdot\nabla)\vec{u} = -\nabla p' + \Delta\vec{u} + (\mathcal{R}\theta + \mathcal{C}\gamma)\vec{k},, \tag{2}$$

$$P_r(\frac{\partial}{\partial t}\theta + \vec{u}\cdot\nabla\theta) = \Delta\theta - \mathcal{R}w, \qquad (t, \vec{x}) \in (0, \infty) \times V \tag{3}$$

$$S_c(\frac{\partial}{\partial t}\gamma + \vec{u}\cdot\nabla\gamma) = \Delta\gamma + \mathcal{C}w, \tag{4}$$

in a subset of L_2, namely ,

$$\mathcal{N} = \{(\vec{u}, p, \theta, \gamma) \in L^2 \mid div\vec{u} = 0; \qquad \frac{\partial u}{\partial z} = \frac{\partial v}{\partial z} = w = 0 \,\mathrm{on}\, \partial \mathrm{V}_2, \tag{5}$$

$$\vec{u} = 0 \,\mathrm{on}\, \partial\mathrm{V}_1 \qquad \theta = \gamma = 0 \,\mathrm{on}\, \partial\mathrm{V}_2 \qquad \frac{\partial\theta}{\partial \mathrm{z}} = -\mathrm{s}\gamma,\ \frac{\partial\gamma}{\partial \mathrm{z}} = \mathrm{r}\gamma \,\mathrm{on}\, \partial\mathrm{V}_1\}.$$

where $\vec{u} = (u, v, w)$, V is a periodicity cell in the x, y-directions, ∂V is the boundary of V, $\partial V_1 = \partial V \cap \{z = 0\}, \partial V_2 = \partial V \cap \{z = 1\}$. The perturbation fields depend on the time t and space $\vec{x} = (x, y, z)$ and $\mathcal{R}^2, \mathcal{C}^2, P_r$ and S_c are the thermal and concentrational numbers of Rayleigh, Prandtl and Schmidt, respectively. In addition, $r, s > 0$ are dimensionless surface reactions numbers.

The basic state S_0 corresponds to the zero solution of the initial-boundary value problem for (2)-(4) in the class $\mathcal{N}$. This state is called non linearly stable if a Liapunov function $E(t)$, called energy, remains bounded when $t \to \infty$ in the sense of $lim_{t\to\infty} \int_0^t E(t')dt' < \infty$ [9], [10]. It is asymptotically nonlinearly stable if $E(t) \to 0$ when $t \to \infty$. The stability or instability of S_0 depends on six physical parameters occurring in (2)-(5): $P_r, S_c = \tau P_r, \mathcal{R}, \mathcal{C}, r$ and s.

3 The evolution equation for the perturbation energy

Integrating over V the sum of the equation (4) multiplied by $P_r^{-1}\gamma$ and the equation (3) multiplied by $S_c^{-1}\theta$ we obtained:

$$\frac{d}{dt}<\theta\gamma>=-\tau\mathcal{R}S_c^{-1}<\gamma w>+\mathcal{C}S_c^{-1}<\theta w>-(1+\tau)S_c^{-1}<\nabla\theta\cdot\nabla\gamma>+ \tag{6}$$

$$S_c^{-1}\int_V\nabla\cdot(\theta\nabla\gamma)dV+P_r^{-1}\int_V\nabla\cdot(\gamma\nabla\theta)dV.$$

Multyplying (2) by $\mathbf{u}$, (3) by θ, (4) by γ and integrating the resulted equations over V and taking into account the boundary conditions from (5) we have respectively

$$\frac{1}{2}\frac{d}{dt}<|\mathbf{u}|^2>=-<|\nabla\mathbf{u}|^2>+\mathcal{R}<\theta w>+\mathcal{C}<\gamma w>, \tag{7}$$

$$\frac{1}{2}\frac{d}{dt}<P_r\theta^2>=-\mathcal{R}<\theta w>-<|\nabla\theta|^2>+\int_V\nabla\cdot(\theta\nabla\theta)dV, \tag{8}$$

$$\frac{1}{2}\frac{d}{dt}<S_c\gamma^2>=\mathcal{C}<\gamma w>-<|\nabla\gamma|^2>+\int_V\nabla\cdot(\gamma\nabla\gamma)dV. \tag{9}$$

We perform the sum of (7) to (8) multiplied by $a>0$, (9) multiplied by $b>0$ and (6) multiplied by $c>0$, and introducing the functions

$$E_2(t)=<|\mathbf{u}|^2+d_1\phi_1^2+d_2\phi_1\phi_2>/2, \qquad \Psi(t)=<d_3\phi_2^2>/2, \tag{10}$$

we obtain

$$\frac{dE_2}{dt}+\frac{d\Psi}{dt}=-<|\nabla\mathbf{u}|^2+(a_1^2d_4+b_1^2d_5+a_1b_1d_6)|\nabla\phi_1|^2+$$

$$(a_2^2d_4+b_2^2d_5+a_2b_2d_6)|\nabla\phi_2|^2+\Big[2a_1a_2d_4+2b_1b_2d_5+(a_1b_2+a_2b_1)d_6\Big]|\nabla\phi_1\cdot\nabla\phi_2|>$$

$$+\mathcal{R}<(a_1d_7+b_1d_8)\phi_1w>+\mathcal{R}<(a_2d_7+b_2d_8)\phi_2w>+$$

$$(aa_1^2+bb_1^2+cS_c^{-1}a_1b_1+cP_r^{-1}a_1b_1)\int_V\nabla\cdot(\phi_1\nabla\phi_1)dV+$$

$$(aa_2^2+bb_2^2+cS_c^{-1}a_2b_2+cP_r^{-1}a_2b_2)\int_V\nabla\cdot(\phi_2\nabla\phi_2)dV+$$

$$(aa_1a_2 + bb_1b_2 + cS_c^{-1}a_1b_2 + cP_r^{-1}a_2b_1)\int_V \nabla\cdot(\phi_1\nabla\phi_2)dV +$$

$$(aa_1a_2 + bb_1b_2 + cS_c^{-1}a_2b_1 + cP_r^{-1}a_1b_2)\int_V \nabla\cdot(\phi_2\nabla\phi_1)dV, \tag{11}$$

where

$$\theta = a_1\phi_1 + a_2\phi_2, \quad \gamma = b_1\phi_1 + b_2\phi_2. \tag{12}$$

Here a_1, a_2, b_1 and b_2 are unknown parameters and d_i, $i = 1\cdots 8$ are functions of a, b, c and the physical parameters, defined by

$$\begin{array}{ll} d_1 = aP_ra_1^2 + bS_cb_1^2 + 2ca_1b_1; & d_2 = aP_ra_1a_2 + bS_cb_1b_2 + c(a_1b_2 + a_2b_1), \\ d_3 = aP_ra_2^2 + bS_cb_2^2 + 2ca_2b_2; & d_4 = a, \\ d_5 = b; & d_6 = cS_c^{-1}(1+\tau), \\ d_7 = 1 - a + c\alpha S_c^{-1}; & d_8 = b\alpha + \alpha - c\tau S_c^{-1}, \end{array}$$

where $\alpha = \frac{\mathcal{C}}{\mathcal{R}}$.

The seven constants a, b, c, a_1, b_1, a_2 and b_2 shall be determined from the requirement that (11) assumes the form [6], [7], [8]

$$\frac{dE_2}{dt} + \frac{d\Psi}{dt} = -<|\nabla\mathbf{u}|^2 + |\nabla\phi_1|^2> + \mathcal{R} <(a_1d_7 + b_1d_8)\phi_1 w>, \tag{13}$$

where the energy E_2 has the form

$$E_2(t) =<|\mathbf{u}|^2 + d_1|\phi_1|^2> /2. \tag{14}$$

In the case $\tau = 1$ the right-hand side of (11) assumes the form from (13) and instead of (10) the energy E_2 assumes the form (14) if

$$\begin{cases} d_2 = 0, \\ a_1^2d_4 + b_1^2d_5 + a_1b_1d_6 = 1, \\ a_2^2d_4 + b_2^2d_5 + a_2b_2d_6 = 0, \\ 2a_1a_2d_4 + 2b_1b_2d_5 + (a_1b_2 + a_2b_1)d_6 = 0, \\ a_2d_7 + b_2d_8 = 0, \\ sb_2 + ra_2 = 0. \end{cases} \tag{15}$$

ϕ_1 and ϕ_2 as linear combinations of θ and γ are given by

$$\phi_1 = a_1'\theta + a_2'\gamma, \qquad \phi_2 = b_1'\theta + b_2'\gamma, \tag{16}$$

where

$$a'_1 = b_2/M, \quad a'_2 = a_2/M, \quad b'_1 = -b_1/M, \quad b'_2 = a_1/M,$$

$$a_1 = b'_2/M', \quad a_2 = -a'_2/M', \quad b_1 = -b'_1/M', \quad b_2 = a'_1/M', \tag{17}$$

and $M = a_1b_2 - a_2b_1$ and $M' = a'_1b'_2 - a'_2b'_1$.

It follows

$$\phi_1 = (b_2\theta - a_2\gamma)/M \qquad \text{and} \qquad \phi_2 = (-\mathrm{b}_1\theta + \mathrm{a}_1\gamma)/\mathrm{M}. \tag{18}$$

The system (15) can be considered as yielding $a_1, b_1, a_2/b_2, b, c$ as functions of a, $(15)_3$ follows from $(15)_1$ and $(15)_2$, so, another relationship between these parameters is necessary.

In order to find it we followed the Joseph's generalized method of parametric differentiation [6], [7], [8].

Denoting

$$2A = \mathcal{R}|a_1d_7 + b_1d_8|, \tag{19}$$

relation (13) implies

$$\frac{dE_2}{dt} \leq -\xi^2\Big(1 - A/\sqrt{R_{a*}}\Big)E_2(t), \tag{20}$$

where [12], [13], [14], [15]

$$\xi^2 = min_{\mathbf{u},\phi_1}\frac{2 < |\nabla\mathbf{u}|^2 + |\nabla\phi_1|^2 >}{< |\mathbf{u}|^2 + |\phi_1|^2 >}, \frac{1}{\sqrt{R_{a*}}} = max_{\mathbf{u},\phi_1}\frac{2 < \phi_1 w >}{< |\nabla\mathbf{u}|^2 + |\nabla\phi_1|^2 >}. \tag{21}$$

Therefore, the stability criterion reads

$$\mathcal{R} < 2\sqrt{R}_{a*}/|a_1d_7 + b_1d_8|. \tag{22}$$

As a consequence $\mathcal{R}$ will be maximal if $|a_1d_7 + b_1d_8|$ will be minimal. Since $|a_1d_7 + b_1d_8|$ is a function of the parameter a this requirement will be fullfilled iff

$$\frac{d(a_1d_7 + b_1d_8)}{da} = 0. \tag{23}$$

This equation represents the equation determining a.

In this way, the stability bound

$$\mathcal{R}_E = 2\sqrt{R}_{a*}/|a_1d_7 + b_1d_8| \tag{24}$$

will be obtained once the system (15), (23), admits real solutions and it can be solved explicitly in terms of the physical parameters.

Of course, all values of the physical parameters ensuring the negativity of $a_1 d_7 + b_1 d_8$ are in the stability domain.

In this section we applied a Joseph's generalized method [6], [7], [8] to derive the evolution equation for E_2.

The Joseph's idea of using (6) was generalized by us in the following way [6], [7], [8]:

We used from the beginning an integral relation, i.e. the equation (6) (already followed by suitable multiplications, addition and integration over V of the balance equations for temperature and concentration (2)-(4)), in [7] we proved that (6) is nothing else but the projection of a system, equivalent to (2)-(4), including the equations which generate (6) and with a symmetrizable linear part, for a suitable choice of the constants [7].

As a consequence, the initial equations (2)-(4) were replaced by some others in which the equations which generated (6) were present. In this way drastically changed the linear part of the initial equations allowing a much more advantageous symmetrization. By contrast, the symmetric operator for (2)-(4) does not contain the effect of terms in $\mathbf{u}$ from (2) and those of terms in θ from (3) because they are opposite.

4 Nonlinear stability bound

From (15) we deduce the relations

$$d_6^2 = 4 d_4 d_5, \tag{25}$$

$$d_8^2 d_4 = d_7^2 d_5, \tag{26}$$

$$\frac{s}{r} = \alpha, \tag{27}$$

Then we determine explicit expression for a_1, b_1 and a_2/b_2in terms of $d_8/d_7, d_6/d_4$ and d_4, or, taking into account (25) and (26), in terms of $\sqrt{d_5/d_4}$ and d_4.This implies

$$a_1 d_7 + b_1 d_8 = d_7/\sqrt{d_4}. \tag{28}$$

On the other hand, (23) was written as an equation of the form

$$\frac{d}{da} \frac{1 + a(\frac{s}{r}\alpha - 1)}{\sqrt{a}} = 0. \tag{29}$$

If $\frac{s}{r}\alpha > 1$, the solution

$$a = \frac{1}{\frac{s}{r}\alpha - 1} \tag{30}$$

of (29) gives, in terms of the physical quantities, the non linear stability bound (24)

$$\mathcal{R}_E = \sqrt{R}_{a*}\Big(\sqrt{(\frac{s}{r})^2 - 1}\Big)^{-1} \tag{31}$$

Theorem. For physical parameters $\mathcal{R}$, $\mathcal{C} = \alpha\mathcal{R}$, $\frac{s}{r} = \alpha$, $(\frac{s}{r})^2 > 1$, *the zero solution of (2)-(4), corresponding to the basic conduction state, is non linearly asymptotically stable if* $\mathcal{R} < \mathcal{R}_E$, *where* $\mathcal{R}_E$ *is given by (31). Or, equivalently, if*

$$\mathcal{C}^2 - \mathcal{R}^2 < R_{a*}$$

where R_{a*} *is given by (21).*

5 Conclusions

We treated the problem of the non linear stability of an equilibrium for a binary mixture in a horizontal layer heated from below and experiencing a catalyzed chemical reaction at bottom plate, using the energy method, improved as in [6] by taking into account an idea from [9] [10] . The given problem governing the perturbation evolution was changed in order to obtain an optimum energy inequation. Then the non linear stability bound was obtained with the aid of some appropriately chosen multiplication constants.

The presence of derivatives in the boundary conditions heavily influences the possibility to relate linear and non linear bounds because of the lack of corresponding maximum principle for the Laplace equation. However, the generalized method, as in [6], [7], [8] gives us the possibility to drastically change the linear problem derived by the evolution equations, so that allows us an easier handling of the linear problem to determine a generalized linearization principle (in the sense of the coincidence of linear and nonlinear stability bounds) [16].

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