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CHEMICAL CONVECTIVE INSTABILITY AND QUASI-EQUILIBRIUM THERMODYNAMICS

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SOMMARIO. Si sviluppa un'analisi non lineare della stabilità per il problema di Bénard relativo ad un fluido chimicamente reagente e riscaldato dall'alto; i risultati sono confrontati con quelli trovati in precedenza da Wollkind & Frisch. Successivamente si elabora un'analisi non lineare della stabilità proprio per il modello di Wollkind & Frisch e si mostra che si possono presentare delle instabilità.

SUMMARY. A nonlinear stability analysis is described for the Bénard problem for a chemically reacting fluid heated from above; the findings are compared with those of Wollkind & Frisch. Next an energy stability analysis is given for the model of Wollkind & Frisch and it is shown that instabilities may occur.

1. INTRODUCTION

In a paper which appeared in 1971 Wollkind and Frisch [1] developed a linear analysis for a chemical instability problem and deduced that for large enough Rayleigh number the Bénard problem involving a chemically dissociating fluid is unstable, in the situation which is stable for the non-reactive fluid, when the fluid layer is heated from above. In addition Wollkind and Frisch gave a plausible physical explanation for the instability result. Although strong instabilities are often present in chemical systems [2], one might suspect that the instability result of Wollkind and Frisch is a direct consequence of their linear approximation but not of the properties of the fluid.

To eliminate this doubt in this paper we develop a nonlinear analysis of the problem investigated in [1]. It is a noticeable result, exhibited in section 2, that the heated above situation is always stable even for not necessarily infinitesimal disturbances. Moreover, in order to explain the apparent contradiction, in section 3 we investigate the reasons which are responsible for the instability result given in [1].

Although the differential system of Wollkind and Frisch has a doubtful applicability to the problem at hand, we think that other stability problems may possess the same features. That is why in section 4 we develop a nonlinear energy stability analysis for their modified system. Coherently with [1], it is shown that, for such a system, instabilities may occur.

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2. ENERGY STABILITY FOR THE HEATED ABOVE CASE

The model with which Wollkind and Frisch commence considers a dissociating fluid contained in the infinite layer $0 < z < d$ and attention is restricted to essentially isochoric motions by adopting a Boussinesq-type approximation. The mass flux through the boundaries $z = 0, d$ is zero and the prescribed temperatures there are T_0, T_1, with $T_1 > T_0$. The relevant equations, (1) - (4) of [1], admit a steady solution in which the velocity is zero, the fraction, α, of free atoms is constant and the temperature, T, is linear in z across the layer.

In non-dimensional form the equations for the perturbation to the constant concentration solution are

$$
\begin{aligned}
&\dot{u}_i = -p_{,i} + \delta_{i3}(R\theta + \phi) + \Delta u_i,\\
&Sc\dot{\phi} = \Delta\phi - X_1\phi, \qquad (1)\\
&Pr\dot{\theta} = -Rw + \Delta\theta + (S + PrA/ScR)\Delta\phi - \frac{X_1 PrA}{ScR}\,\phi,
\end{aligned}
$$

where $\mathbf{u}$, θ, ϕ, p are the perturbation fields of velocity (solenoidal), temperature, fraction of free atoms and pressure, R^2 is the Rayleigh number, Δ is the three-dimensional Laplacian, a superposed dot denotes the material derivative, $w = u_3$ and where for completeness we include below the non-dimensionalization appropriate to the notation of [1]:

$$Sc = \nu/D_{12}^0, \quad X_1 = d^2/\tau D_{12}^0, \quad \kappa = \lambda^0/\rho_0 c_1,$$
$$Pr = \nu/\kappa, \quad S = D_{12}^0 D_0/2mc_1\kappa, \quad A = c_2\alpha/c_1 b.$$

The functions $\mathbf{u}$, θ, ϕ, p are assumed periodic in x, y and satisfy the boundary conditions

$$\mathbf{u} = 0, \quad \frac{\partial\phi}{\partial z} = 0, \quad \theta = 0, \qquad (2)$$

on $z = 0, d$.

To investigate nonlinear stability we now define, for $\lambda (> 0)$ to be chosen, an energy $E_\lambda(t)$ by

$$E_\lambda(t) = 1/2\,(\|u\|^2 + Pr\|\theta\|^2 + \lambda Sc\|\phi\|^2), \qquad (3)$$

where $\|\,.\,\|$ denotes the norm on the Hilbert space $L^2(V)$, V being a period cell of the perturbed solution. The idea of coupling constants, i.e. λ in (3), in energy theory was developed extensively by D.D. Joseph (see e.g. [3]) and leads to a very powerful method for determining when a system is *stable* as opposed to standard linear theory which only yields information on instability. Such a stability boundary may then be used to find the parameter region in which subcritical instabilities may occur.

In this work, the independence of equation $(1)_2$, allows us to use λ in a different way from the normal theory of the best λ [3]. Let D(.) denote the Dirichlet integral of a quantity and then from (1) we may derive

$$\dot{E}_\lambda = \langle \phi, w \rangle - D(u) - \lambda D(\phi) - D(\theta) - \lambda X_1 \| \phi \|^2$$
$$- \left(S + \frac{PrA}{ScR} \right) D(\phi, \theta) - \frac{X_1 PrA}{ScR} \langle \phi, \theta \rangle. \tag{4}$$

From use of the arithmetic-geometric mean and Poincaré inequalities we next establish the following estimates,

$$\langle \phi, w \rangle \leqq 1/2\, \lambda_1 \| w \|^2 + 1/2\, \lambda_1^{-1} \| \phi \|^2,$$
$$- \left(S + \frac{PrA}{ScR} \right) D(\theta, \phi) \leqq \frac{1}{3} D(\theta) + \frac{3}{4} \left(S + \frac{PrA}{RSc} \right)^2 D(\phi),$$
$$\frac{X_1 PrA}{RSc} \langle \phi, \theta \rangle \leqq \frac{1}{3} D(\theta) + \frac{3 (X_1 PrA)^2}{4 \lambda_1 (RSc)^2} \| \phi \|^2,$$

where λ_1 is the constant in Poincaré's inequality $\lambda_1 \| w \|^2 \leqslant \leqslant \| \nabla w \|^2$. These estimates are used in (4) and we then select λ so large that

$$\lambda \geqq \frac{3}{4} \left(S + \frac{PrA}{RSc} \right)^2 \text{ and } \lambda X_1 \geqq \lambda_1^{-1} + \frac{3}{2\lambda_1} \left(\frac{X_1 PrA}{RSc} \right)^2,$$

and from the resulting inequality and further use of Poincaré's inequality we obtain

$$\dot{E}_\lambda \leqq -M E_\lambda,$$

where

$$M = \min\{\lambda_1, 2\lambda_1/3Pr, X_1/Sc\}.$$

Clearly then, $E_\lambda \to 0$, $t \to \infty$, and so there is *no* instability when the fluid layer is heated from above. (Such a conclusion was suggested by Wollkind and Bdzil [4], although their evidence was presumably based on linear theory).

3. EXPLANATION OF THE APPARENT CONTRADICTION

For the heated above case it remains to explain why Wollkind and Frisch predicted instability. The reason is that they postulated ad hoc relations between α and T of the form $\dot{\alpha} = \Phi \dot{T}$, $\Delta\alpha = \Phi \Delta T$, for a constant Φ; relations which they attribute to a modification of Lighthill's model [5]. However, Lighthill derives a differential relationship connecting α, p and T in changes between states of equilibrium and uses this to eliminate the *gradients* of α and p to simplify the heat and mass flux expressions. In [1] such a relationship is extended to include *time derivatives;* we believe that great care must be exercised with such quasi-equilibrium approximations when dealing with time derivatives, an assertion borne out by our energy stability analysis. It is convenient at this point to cite Truesdell and Toupin [6], pp. 649 - 650, who in their account of differential relationships in a chemical reacting mixture assert: *While writers on «irreversible thermodynamics» sometimes use the relations of this section in problems concerning deformation, we are unable to find any solid ground for ascribing any relevance to them except in equilibrium.*

In the light of these remarks the present work assumes much relevance as one interpretation is that it provides solid ground against their employment in contexts involving deformation.

The work of Wollkind and Frisch [1], concerns a mathematically interesting system which is likely to model other stability problems. This motivates the energy stability analysis which is given in next section. In fact we find a nonlinear energy boundary which complements well the linear analysis of [1] and determines a close band of Rayleigh numbers for which subcritical bifurcation may be possible. As far as we are aware this is the first time a fully nonlinear energy analysis has been used to suggest instabilities may occur when a system is heated from above.

4. AN ENERGY ANALYSIS FOR THE MODIFIED SYSTEM

A perturbation to the constant concentration equilibrium solution for the *modified* system of [1] (using the same chemical quasi-equilibrium approximation) satisfies the equations

$$\dot{u}_i = -p_{,i} + g\alpha k_i \theta + gbk_i \phi + \nu \Delta u_i,$$
$$\dot{\theta} = \beta w + \kappa \Delta \theta, \tag{5}$$
$$\dot{\theta} = \beta w - M\phi + D_{12}^0 \Delta \theta,$$

for divergence free $\mathbf{u}$. The constant coefficients are in the notation of [1] and we do not include them explicitly as we give a non-dimensional version, which corresponds to our notation, below. A key factor is that from $(5)_{2,3} \phi = = \Delta\theta [(D_{12}^0 - \kappa)/M]$ and hence ϕ may be eliminated to yield the following (non-dimensional) equations:

$$\dot{u}_i = -p_{,i} + \delta_{i3} R(\theta + \epsilon B \Delta \theta) + \Delta u_i,$$
$$Pr \dot{\theta} = -Rw + \Delta\theta, \tag{6}$$

in which ϵB is a reaction term, of small magnitude, introduced in [1].

It is interesting to observe that the ϵB term in (6) is a term which would make that system non-symmetric even in the heated below case. We may expect, therefore, from the work of Galdi and Straughan [7] that the energy and linear critical Rayleigh numbers will *not* be the same.

To investigate the stability of the zero solution to (6), we choose

$$E(t) = 1/2 \| u \|^2 + 1/2\, Pr \| \theta \|^2. \tag{7}$$

The energy equation appropriate to (7) is determined to be

$$\dot{E} = RI - \mathscr{D}, \tag{8}$$

where

$$\mathscr{D} = D(u) + D(\theta). \qquad I = -\epsilon B D(\theta, w).$$

Define now

$$\frac{1}{R_E} = \max \frac{I}{\mathscr{D}} \; (= \lambda), \tag{9}$$

where the maximum is over the space of admissible solutions and from (8)

$$\dot{E} \leqq - \mathscr{D} R \left(\frac{1}{R} - \frac{1}{R_E} \right) \tag{10}$$

If now $R < R_E$, (10) and Poincaré's inequality show that $E \to 0$ exponentially, as $t \to \infty$.

The problem is then to find R_E, or equivalently λ, as in (9). To this end we derive the Euler-Lagrange equations for this maximum as,

$$\begin{aligned} &\epsilon B \delta_{i3} \Delta\theta + 2\lambda \Delta u_i = 2p_{,i}, \\ &\epsilon B \Delta w + 2\lambda\Delta\theta = 0. \end{aligned} \tag{11}$$

These equations are linear and so we may use a normal mode technique to obtain

$$4\lambda^2 (D^2 - a^2)^2 W = - a^2 (\epsilon B)^2 (D^2 - a^2) W \tag{12}$$

where $D = d/dz$, a^2 is the wave number and $W(z)$ is the z part of u_3. For the two free boundaries situation covered in [1] the boundary conditions allow W to be composed of $\sin m\pi z$, $m = 1, 2, \ldots$, and (12) yields

$$\lambda^2 = \frac{(\epsilon B)^2 a^2}{4(m^2\pi^2 + a^2)} \tag{13}$$

Obviously, as a function of m, λ is maximum for $m = 1$. We then see that the maximum of λ is achieved aymptotically as $a^2 \to \infty$. We may, therefore, conclude that $R_E = 2/\epsilon B$.

If we denote by R_L^2 the critical Rayleigh number of linear theory, the asymptotic expression given in [1], eq. (36), is

$$R_L^2 = \frac{4}{(\epsilon B)^2} + \frac{2\pi^2}{\epsilon B} + 0(1), \tag{14}$$

which compares with the energy limit

$$R_E^2 = \frac{4}{(\epsilon B)^2} \tag{15}$$

Estimates (14) and (15), which agree to leading order, determine quantitatively a band of Rayleigh numbers where subcritical bifurcation may occur.

The discussion just completed is concerned with the situation in which the fluid layer is heated from above and clarifies what might have appeared to be an anomaly between the present work and that of Wollkind and Frisch [1].

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