### THERMODYNAMIC ANALYSIS OF INVERTED BIFURCATION

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### ABSTRACT

We present a thermodynamic analysis of inverted bifurcation in binary mixtures heated from below. From this analysis it follows that an inverted bifurcation is caused by the competition between a stabilizing effect with a long relaxation time and a destabilizing effect with a short relaxation time. These conditions are precisely the same as those that give rise to overstability. This might explain why overstability and inverted bifurcation occur in the same systems.

### INTRODUCTION

The onset of convection in a layer of pure liquid heated from below, the so-called Bénard-Rayleigh instability, has been extensively investigated for a long time (for reviews see Refs. 1 and 2). In recent years there has been considerable interest in thermal convection effects in horizontal layers of binary mixtures (3) and nematic liquid crystals (4). The Bénard-Rayleigh instability in these systems exhibits features that are dramatically different from those observed in pure isotropic liquids. most spectacular effects have been observed in binary mixtures where the Soret effect causes the more dense component to move to the warm boundary and in homeotropic nematics with a positive heat conduction anisotropy. These systems become unstable to stationary convection when heated from above even though the overall density gradient is not adverse (5,6). Furthermore when heated from below these systems become unstable to oscillatory convection (overstability) and finite amplitude convection (7,9) (inverted bifurcation).

Previously we pointed out that overstability is due to the competition between a stabilizing effect with a long relaxation time and a destabilizing (10,11) effect with a short relaxation time. The fact that overstability and inverted bifurcation occur together in such disparate systems as binary mixtures and nematic liquid crystals suggests that inverted bifurcation is also due to the difference in time scales between the stabilizing and destabilizing effect. In this paper we show that this is indeed the case for a binary mixture.

Overstability and inverted bifurcation in binary mixtures have been studied numerically by Platten and Chavepeyer (12,13) and quite recently also by Velarde and Antoranz (14,15). The aim of the present work is not so much quantitative but rather to elucidate the basic physical mechanism that gives rise to an inverted bifurcation.

### CLASSIFICATION OF INSTABILITIES

A convenient starting point for the classification of instabilities is the Landau expansion (16) of the rate of change of the kinetic energy of a convective disturbance.

$$E_{kin} = a(R-R_c)v^2 + Bv^4 + Cv^6 + \dots$$
 (a > 0) (1)

Here v is the amplitude of the convective disturbance, R is a parameter characterizing the non-equilibrium constraints on the system (Reynolds number, Rayleigh number, Taylor number ...) and  $R_{\rm c}$  is the value of this parameter for which the system becomes unstable (critical value). In the stationary state there is a balance between the rate of injection of energy into the convective disturbance and the rate of viscous dissipation of kinetic energy associated with the convective disturbance

$$\dot{E}_{kin} = 0 \tag{2}$$

In case the coefficient B is negative and large the higher order terms in the expansion (1) are irrelevant and one obtains from (2)

$$v = 0$$
 for  $R < R_c$   
 $V = const. (R-R_c)^{1/2}$  for  $R > R_c$ 

This case is commonly referred to as a direct or normal bifurcation and is analogous to a second order (continuous) phase transition. The behaviour of v as a function of R is schematically represented in fig. 1. The above theoretical prediction for the behaviour of

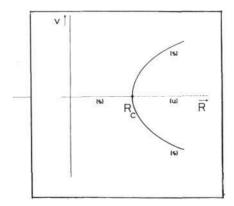


Fig. 1. Schematic representation of the variation of the amplitude of the velocity for a direct bifurcation
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the amplitude of the convective disturbance, originally due to Landau, has been experimentally verified for the Bénard-Rayleigh instability (17) and the Taylor instability (18) using light scattering techniques.

A different situation arises when B is positive. Now the coefficient C must be negative to ensure that (2) can be satisfied. In this case (2) has already solutions  $v \neq 0$  for  $R \geqslant R_0$  where

$$R_{O} = R_{C} - \frac{B}{4a|C|}$$

(subcritical finite amplitude instability) and the system exhibits a hysteresis loop between  $R_{\rm O}$  and  $R_{\rm C}$  (see fig.2). This case is known as inverted bifurcation and is analogous to a first order (discontinuous) transition.

The cross over between direct and inverted bifurcation takes place for B = 0. In this case

$$v = 0$$
 for  $R < R_c$   
 $v = const.(R-R_c)^{1/4}$  for  $R > R_c$ 

This situation is analogous to a tricritical point in equilibrium phase transitions (19).

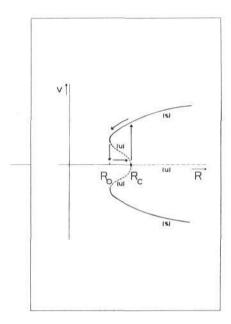


Fig. 2. Schematic representation of the variation of the amplitude of the velocity and hysteresis loop for an inverted bifurcation

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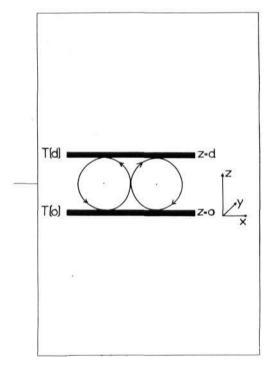


Fig. 3. Schematic representation of the velocity perturbation.

and d is the thickness of the fluid layer. As a preliminary to the calculation of  $\mathrm{E_{kin}}$  for a binary mixture we first consider a pure fluid. The rate of viscous dissipation of kinetic energy per unit volume is given by

$$\dot{E}_{kin}^{v} = -\frac{1}{V} \frac{1}{2} \eta \int \left( \frac{\partial v_{i}}{\partial x_{j}} + \frac{\partial v_{j}}{\partial x_{i}} \right)^{2} dV$$

$$= -2 \eta q^{2} v^{2} \tag{4}$$

where

$$q^2 = q_x^2 + q_z^2$$

and  $\eta$  is the shear viscosity. The rate of production of kinetic energy by the buoyancy force per unit volume is given by

$$\dot{\mathbf{E}}_{kin}^{g} = -\frac{1}{V} \int \mathbf{g} \, \delta \rho \, \mathbf{v}_{z} \, dV \tag{5}$$

where g is the gravitation constant and  $\delta\rho$  is the perturbation in the mean steady-state density distribution. For a pure fluid we can write

$$\delta \rho = -\rho \alpha \delta T \tag{6}$$

where  $\delta T$  is the perturbation in the mean steady-state temperature distribution and  $\alpha$  is the thermal expansivity. The perturbation  $\delta T$  is determined by

$$v_{z} = \frac{d < T >}{dz} = \chi \nabla^{2} \delta T \tag{7}$$

where  $\chi$  is the thermal diffusivity and <T> is the mean steady-state temperature distribution (<...> denotes an average over the horizontal plane). Following the work of Chandrasekhar (22) one obtains to order  $v^2$  for the mean steady-state temperature distribution

# INVERTED BIFURCATION IN BINARY MIXTURES

The fundamental physical process that lies at the origin of the Bénard-Rayleigh instability is the conversion of energy released by the buoyancy force into kinetic energy of the convective motion (20). Stationary convection sets in when the rate of injection of energy by the buoyancy force acting on the fluid  $(E_{kin}^g)$ 

begins to balance the rate of viscous dissipation of energy  $(\dot{E}_{\text{kin}}^{\text{V}})$ 

$$\dot{E}_{kin} = \dot{E}_{kin}^{v} + \dot{E}_{kin}^{g} = 0$$

when the convective disturbance has a finite amplitude, convective transport causes a modification of the mean (horizontally-averaged) temperature and concentration distribution. This in turn modifies the rate of liberation of thermodynamically available energy by the buoyance force acting on the fluid (21,22).

For the sake of simplicity we consider a convective disturbance in the form of a circular roll pattern (see Fig.3).

$$v_{x} = -2v \sin q_{x} x \cos q_{z} z$$

$$v_{y} = 0$$

$$v_{z} = 2v \cos q_{x} x \sin q_{z} z$$
(3)

Here

$$q_x = q_z = \frac{\pi}{d}$$

$$\frac{d < T>}{dz} = -\beta \left\{ 1 + \frac{v^2}{v^2 q^2} \cos 2 q_z z \right\}$$
 (8)

where

$$\beta = \{T(z=0) - T(z=d)\} / d$$

The second term on the r.h.s. of (8) represents the modification of the temperature gradient due to convective heat transport. Substituting the temperature distribution (8) in (7) one obtains

$$\delta T = \frac{\beta}{\chi q^2} 2v \{\cos q_x \times \sin q_z z - \frac{v^2}{\chi^2 q^2} (\frac{1}{5} \cos q_x \times \sin q_z z + \frac{2}{5} \cos q_x \times \sin^3 q_z z)\}$$
(9)

Using (9) in (6) one obtains for the rate of production of kinetic energy by the buoyancy force

$$\dot{E}_{kin}^{g} = \frac{g \rho \alpha \beta v^{2}}{\chi q} \left\{ 1 - \frac{v^{2}}{2\chi^{2}q^{2}} \right\}$$
 (10)

where  $\delta c$  is the perturbation in the mean steady-state concentration distribution and  $\alpha'$  is the solutal expansivity. The perturbation  $\delta c$  is determined by

$$v_{z} \frac{d \langle c \rangle}{dz} = D \nabla^{2} \delta c \tag{13}$$

where D is the mass diffusion coefficient and <c> is the mean steady-state temperature distribution. Using the same line of reasoning as used in the calculation of the mean temperature distribution one obtains

$$\frac{d < c >}{dz} = \frac{k_T^{\beta}}{T} \{1 - \frac{2v^2}{D^2q^2} \sin^2 q_z z\}$$
 (14)

where  $k_T$  is the thermal diffusion ratio. The first term on the r.h.s. of (14) represents the Soret driven concentration gradient and the second term represents the modification of this concentration gradient due to convective mass transport. Substituting Combining (4) and (10) one obtains for the rate of change of the kinetic energy of the convective disturbance (3)

$$\dot{\mathbf{E}}_{kin} = \mathbf{a}(\mathbf{R} - \mathbf{R}_c) \mathbf{v}^2 + \mathbf{B} \mathbf{v}^4 \tag{11}$$

where

$$a = \frac{\eta}{d^4q^2}$$

$$R = \frac{g \alpha \beta d^4}{\chi^{V}}$$
 (Rayleigh number)
$$R_c = 2q^4d^4$$
 (critical Rayleigh number)
$$B = -\frac{g \rho \alpha \beta}{2\chi^3q^4}$$

Here  $\nu$  is kinematic viscosity. We see that B is negative and thus at R = R<sub>c</sub> the system will undergo a continuous transition to the convective state (direct bifurcation).

In the case of a binary mixture the perturbation in the mean steady-state density distribution can be written as

$$\delta \rho = -\rho \alpha \delta T + \rho \alpha' \delta c \tag{12}$$

the concentration distribution (14) in (13) one obtains

$$\delta c = -\frac{k_{\rm T}}{Dq^2} \beta 2v \{\cos q_{\rm x} \times \sin q_{\rm z}z - \frac{v^2}{D^2q^2} (\frac{6}{5}\cos q_{\rm x} \times \sin q_{\rm z}z + \frac{2}{5}\cos q_{\rm x} \times \sin^3 q_{\rm z}z)\}$$
(15)

Using (9) and (15) in (12) one now obtains for the rate of production of kinetic energy by the buoyancy force

$$\dot{E}_{kin}^{g} = \frac{g\rho\alpha\beta}{q^{2}} (\frac{1}{\chi} + \frac{S}{D})v^{2} - \frac{g\rho\alpha\beta}{2q^{4}} (\frac{1}{\chi^{3}} + \frac{3S}{D^{3}}) v^{4}$$
 (16)

The dimensionless parameter

$$S = \frac{k_T}{T} \frac{\alpha'}{\alpha}$$

is negative in case the heavy component moves to the warm boundary. Combining (4) and (16) one obtains for the rate of change of the kinetic energy of the convective disturbance (3) in a binary mixture

$$\dot{E}_{kin} = a(R-R_c)v^2 + Bv^4$$

where

$$a = \frac{\eta}{d^4 q^2} \left(1 + \frac{S\chi}{D}\right)$$

$$R = \frac{g \alpha \beta d^4}{\chi \nu}$$

$$R_{C} = 2q^{i_{4}}d^{i_{4}} \frac{1}{1 + \frac{S\chi}{D}}$$

$$B = -\frac{g\rho\alpha\beta}{2q^4} \left(\frac{1}{\chi^3} + \frac{3S}{D^3}\right)$$

It is clear that for binary mixture heated from below where the more dense component moves to the warm boundary (S < 0) the Soret effect to lowest order in v has a stabilizing influence i.e. it leads to an increase of  $R_{\rm C}$ . Let us now consider the coefficient B, the sign of which determines whether we are dealing with a direct bifurcation (B < 0). The coefficient B contains two distinct contributions of opposite sign. The negative contribution

$$-\frac{g\rho\alpha\beta}{2\chi^3q^4}$$

is due to the fact that convection changes the mean temperature distribution in such a way that the rate of transfer of energy from the gravitational field to the convective disturbance is lowered. The positive contribution

$$\frac{-3g\rho\alpha\beta}{2D^3a^4}$$

is due to the fact that convection stirs up the Soret driven concentration gradient there by lowering its stabilizing effect. Since for liquid mixtures  $D \ll \chi$  the effect of convection on the stabilizing concentration gradient is much larger than on the destabilizing temperature gradient. The result is that for values of S smaller than  $\frac{1}{3} \frac{D^3}{\gamma^3}$  the positive term in B dominates and thus

for these values of S the system will exhibit an inverted bifurcation.

# CONCLUSION

The inverted bifurcation in a binary mixture heated from below where the more dense component moves to the warm boundary is due to the competition of a stabilizing effect with a long relaxation time and a destabilizing effect with a short relaxation time. Precisely the same conditions give rise to overstability. Actually oscillatory convection and finite amplitude convection lead in different ways to the same result i.e. both effectively eliminate the slow stabilizing effect while retaining the fast destabilizing effect.

It would be of interest to study the cross over between direct and inverted bifurcation experimentally. In binary liquids D/ $\chi$  is typically  $10^{-2}$  and thus the cross over takes place for S  $\simeq$  -  $10^{-6}$  which is experimentally hard to realize. A system that may offer better chances to perform the appropriate experiments is a homeotropic nematic with positive heat conduction anisotropy

heated from below. Here it is possible to change the ratio of the relevant relaxation times with a stabilizing magnetic field (9) which could induce the cross over between direct and inverted bifurcation.

#### ACKNOWLEDGEMENT

This work was initiated by stimulating discussions with E. Guyon.

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Here v is the amplitude of the convective disturbance, R is a parameter characterizing the non-equilibrium constraints on the system (Reynolds number, Rayleigh number, Taylor number  $\dots$ ) and  $R_c$  is the value of this parameter for which the system becomes unstable (critical value). In the stationary state there is a balance between the rate of injection of energy into the convective disturbance and the rate of viscous dissipation of kinetic energy associated with the convective disturbance

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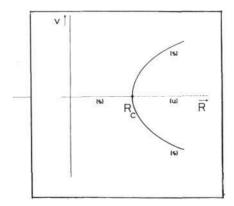


Fig. 1. Schematic representation of the variation of the amplitude of the velocity for a direct bifurcation
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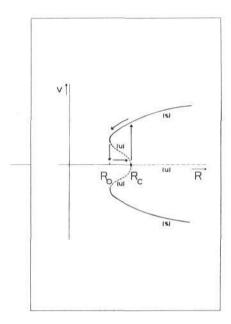


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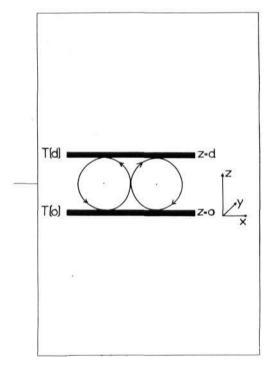


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Using (9) and (15) in (12) one now obtains for the rate of production of kinetic energy by the buoyancy force

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The dimensionless parameter

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where

$$a = \frac{\eta}{d^4 q^2} \left(1 + \frac{S\chi}{D}\right)$$

$$R = \frac{g \alpha \beta d^4}{\chi \nu}$$

$$R_{C} = 2q^{i_{4}}d^{i_{4}} \frac{1}{1 + \frac{S\chi}{D}}$$

$$B = -\frac{g\rho\alpha\beta}{2q^4} \left(\frac{1}{\chi^3} + \frac{3S}{D^3}\right)$$

It is clear that for binary mixture heated from below where the more dense component moves to the warm boundary (S < 0) the Soret effect to lowest order in v has a stabilizing influence i.e. it leads to an increase of  $R_{\rm C}$ . Let us now consider the coefficient B, the sign of which determines whether we are dealing with a direct bifurcation (B < 0). The coefficient B contains two distinct contributions of opposite sign. The negative contribution

$$-\frac{g\rho\alpha\beta}{2\chi^3q^4}$$

is due to the fact that convection changes the mean temperature distribution in such a way that the rate of transfer of energy from the gravitational field to the convective disturbance is lowered. The positive contribution

$$\frac{-3g\rho\alpha\beta}{2D^3a^4}$$

is due to the fact that convection stirs up the Soret driven concentration gradient there by lowering its stabilizing effect. Since for liquid mixtures  $D \ll \chi$  the effect of convection on the stabilizing concentration gradient is much larger than on the destabilizing temperature gradient. The result is that for values of S smaller than  $\frac{1}{3} \frac{D^3}{\gamma^3}$  the positive term in B dominates and thus

for these values of S the system will exhibit an inverted bifurcation.

# CONCLUSION

The inverted bifurcation in a binary mixture heated from below where the more dense component moves to the warm boundary is due to the competition of a stabilizing effect with a long relaxation time and a destabilizing effect with a short relaxation time. Precisely the same conditions give rise to overstability. Actually oscillatory convection and finite amplitude convection lead in different ways to the same result i.e. both effectively eliminate the slow stabilizing effect while retaining the fast destabilizing effect.

It would be of interest to study the cross over between direct and inverted bifurcation experimentally. In binary liquids D/ $\chi$  is typically  $10^{-2}$  and thus the cross over takes place for S  $\simeq$  -  $10^{-6}$  which is experimentally hard to realize. A system that may offer better chances to perform the appropriate experiments is a homeotropic nematic with positive heat conduction anisotropy

heated from below. Here it is possible to change the ratio of the relevant relaxation times with a stabilizing magnetic field (9) which could induce the cross over between direct and inverted bifurcation.

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