

12. Non-Equilibrium Phase Transitions

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12.A. Introduction

This chapter deals with phase transitions in systems that are far from absolute thermodynamic equilibrium. To keep the problem manageable, we shall consider only chemical and hydrodynamic systems that can be described in terms of thermodynamic densities that are sufficiently well-behaved functions of space and time. Physically, this means the systems are in local equilibrium and the time scales of interest are large compared to any local relaxation times.

If a system is moved far enough away from absolute equilibrium, nonlinear effects become dominant. Now, nonlinear equations can admit multiple solutions that have different regions of stability. This means, by changing the parameters of a nonlinear system, we can induce transitions between phases represented by the stable solutions.

In the linear regime near absolute equilibrium, the stable state is a steady state characterized by minimum entropy production if one of the thermodynamic forces is held fixed. This state is said to be on the **thermodynamic branch**.

Nonequilibrium phase transitions occur when the thermodynamic branch becomes unstable. If space-time symmetries are broken during the transition, the new state may exhibit oscillatory pattern in space and/or time. These patterns are called **dissipative structures** since energy, and sometimes matter, must be supplied to maintain them.

Simple models of nonequilibrium phase transitions to be discussed are

1. Chemical systems
 - (a) Schlogl model with 1st order-like phase transition.
 - (b) Brusselator model with dissipative structures.
2. Hydrodynamic systems
 - (a) Rayleigh-Benard instability.

12.B. Non-Equilibrium Stability Criteria

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12.B.0. Entropy Production

A nonequilibrium system is dissipative since, to satisfy the 2nd law, there must be some mechanisms that increase its entropy more than that offered by the spontaneous decay to absolute equilibrium. Thus, stability conditions are related to the rate of entropy production.

To begin, consider a closed, isolated, hydrodynamic system of constant V . The total time rate of change of entropy of the system is given by integrating over V the entropy balance equation

$$\frac{\partial \rho s}{\partial t} = -\nabla \cdot (\rho s \mathbf{v} + \mathbf{J}_s^D) + \sigma_s \quad (10.24)$$

to get

$$\begin{aligned} \frac{dS}{dt} &= \int_V dV \frac{\partial \rho s}{\partial t} = -\int_V dV \nabla \cdot (\rho s \mathbf{v} + \mathbf{J}_s^D) + \int_V dV \sigma_s \\ &= -\oint_A d\mathbf{A} \cdot (\rho s \mathbf{v} + \mathbf{J}_s^D) + \int_V dV \sigma_s \end{aligned} \quad (12.1)$$

$$= \int_V dV \sigma_s \quad (12.2)$$

where A is the surface bounding V and the surface integral in (12.1) vanishes because the system is closed and isolated. The 2nd law becomes

$$\frac{dS}{dt} = \int_V dV \sigma_s \geq 0 \quad (12.3)$$

which can be satisfied if the local entropy production σ_s is nonnegative.

According to (10.179), we can write

$$\sigma_s = -\sum_i J_i \chi_i \geq 0 \quad (12.4)$$

where J_i is a local flux and χ_i the corresponding local force.

12.B.1. Stability Conditions Near Equilibrium

Near equilibrium in the linear regime, we can write

$$J_i = -\sum_j L_{ij} \chi_j \quad (12.5)$$

where $L_{ij} = L_{ji}$ (Onsager's relation). Putting (12.5) into (12.4) gives

$$\sigma_s = \sum_{i,j} L_{ij} \chi_i \chi_j \geq 0 \quad (12.6)$$

which means the symmetric matrix $\mathbf{L} = (L_{ij})$ is non-negative. Furthermore, for spontaneous processes, it is positive definite. The necessary condition for minimum entropy production is

$$\begin{aligned} 0 &= \frac{\partial \sigma_s}{\partial \chi_k} = \sum_{i,j} L_{ij} (\delta_{ik} \chi_j + \delta_{jk} \chi_i) = \sum_j L_{kj} \chi_j + \sum_i L_{ik} \chi_i \\ &= \sum_i (L_{ki} + L_{ik}) \chi_i \\ &= 2 \sum_i L_{ki} \chi_i = -2J_k \end{aligned} \quad (12.12)$$

Thus, if there is no constraint on the system, all χ_i are independent and we have

$$J_i = 0 \quad \text{for all } i$$

which is just the absolute equilibrium state. On the other hand, if k of the forces, say,

$\{\chi_i, i = 1 \cdots k\}$ are held fixed, the necessary conditions for minimum entropy

production in a system subject to n forces are

$$J_i = 0 \quad \text{for } i = k+1, \dots, n \quad (12.13)$$

When the minimum entropy production state is reached, the system becomes

stationary so that the k fluxes $\{J_i, i = 1, \dots, k\}$ will become constant. Such a state is

called a k th order stationary state. Near this steady state, we can write

$$\begin{aligned} \sigma_s(\chi_{k+1}, \dots, \chi_n) &= \sigma_s(\chi_{k+1}^0, \dots, \chi_n^0) + \sum_{i=k+1}^n \left(\frac{\partial \sigma_s}{\partial \chi_i} \right)^0 \delta \chi_i \\ &\quad + \frac{1}{2} \sum_{i=k+1}^n \sum_{j=k+1}^n \left(\frac{\partial^2 \sigma_s}{\partial \chi_i \partial \chi_j} \right)^0 \delta \chi_i \delta \chi_j + \dots \end{aligned}$$

where the subscript 0 denotes steady state values. Using (12.12), we have

$$\sigma_s(\chi_{k+1}, \dots, \chi_n) = \sigma_s(\chi_{k+1}^0, \dots, \chi_n^0) + \frac{1}{2} \sum_{i=k+1}^n \sum_{j=k+1}^n L_{ij} \delta\chi_i \delta\chi_j + \dots \quad (12.14)$$

The quantity

$$\Delta P = \frac{1}{2} \int dV \sum_{i,j=k+1}^n L_{ij} \delta\chi_i \delta\chi_j > 0 \quad (12.15)$$

is called the **excess entropy production**. It is positive definite since \mathbf{L} is. Since the steady state is the minimum entropy production state, we have

$$\begin{aligned} \frac{d\Delta P}{dt} &= \int dV \sum_{i,j=k+1}^n L_{ij} \delta\chi_i \frac{d\delta\chi_j}{dt} = - \int dV \sum_{j=k+1}^n \delta J_j \frac{d\delta\chi_j}{dt} \\ &= - \int dV \sum_{j=k+1}^n g_{ij} \delta J_i \delta J_j \leq 0 \end{aligned} \quad (12.16)$$

where we've used [see section 10.D],

$$\delta = \mathbf{L}^{-1} \cdot \mathbf{M} \cdot \delta = \mathbf{g} \cdot \delta \quad \text{and} \quad \delta \mathbf{J} = \frac{d\delta}{dt}$$

Thus, ΔP is a Liapounov function [see Appendix C].

Note that (12.15,16) are stability criteria for steady states in the linear regime. They need not be satisfied by steady states in the nonlinear regime.

12.B.2. Stability Conditions Far From Equilibrium

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12.B.2.1. General Arguments

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12.B.2.1.1. Stability Relation

Using (12.4), the total entropy production can always be written as

$$P = -\int dV \sum_i J_i \chi_i \quad (12.17)$$

Taking the time derivative gives

$$\frac{\partial P}{\partial t} = -\int dV \sum_i \left(\frac{\partial J_i}{\partial t} \chi_i + J_i \frac{\partial \chi_i}{\partial t} \right) \quad (12.18)$$

$$= \frac{\partial_\chi P}{\partial t} + \frac{\partial_J P}{\partial t} \quad (12.18a)$$

where

$$\frac{\partial_\chi P}{\partial t} = -\int dV \sum_i J_i \frac{\partial \chi_i}{\partial t} \quad (12.18b)$$

$$\frac{\partial_J P}{\partial t} = -\int dV \sum_i \frac{\partial J_i}{\partial t} \chi_i \quad (12.18c)$$

In the linear regime where $J_i = \sum_j L_{ij} \chi_j$ with $L_{ij} = L_{ji}$, we have

$$\sum_i \frac{\partial J_i}{\partial t} \chi_i = \sum_{ij} L_{ij} \frac{\partial \chi_j}{\partial t} \chi_i = \sum_{ij} L_{ji} \frac{\partial \chi_i}{\partial t} \chi_j = \sum_i J_i \frac{\partial \chi_i}{\partial t}$$

so that (12.18) implies

$$\frac{\partial_\chi P}{\partial t} = -\int dV \sum_i J_i \frac{\partial \chi_i}{\partial t} = \frac{1}{2} \frac{\partial P}{\partial t} \leq 0 \quad (12.19)$$

where the inequality is obtained from (12.16).

In the nonlinear regime, we still have (proof shown later)

$$\frac{\partial_\chi P}{\partial t} = -\int dV \sum_i J_i \frac{\partial \chi_i}{\partial t} \leq 0 \quad (12.20)$$

but there is no general constraint on $\frac{\partial_J P}{\partial t}$. Stability analysis of the system therefore

requires, besides (12.20), one more relation.

12.B.2.1.2. Example: Chemical System

Consider a chemically reacting system of N types of molecules held far from equilibrium by its large affinity. We shall assume both pressure and temperature to be uniform throughout the system so that all effects of diffusion, viscosity, and thermal conduction can be neglected. The entropy production thus simplifies to

$$P = -\frac{1}{T} \int dV \sum_{\alpha=1}^r J_{\alpha}^c A_{\alpha} \quad (12.22)$$

[see (10.179)], where r is the number of reactions. Therefore

$$\frac{\partial_{\chi} P}{\partial t} = -\frac{1}{T} \int dV \sum_{\alpha=1}^r J_{\alpha}^c \frac{\partial A_{\alpha}}{\partial t} \quad (12.23)$$

From (10.179), we can write the balance equation for the j th kind of molecules as

$$\frac{\partial c_j}{\partial t} = \sum_{\alpha=1}^r \nu_{j\alpha} J_{\alpha}^c \quad (12.24)$$

Using the definition of the affinity

$$A_{\alpha} = \sum_{j=1}^N \nu_{j\alpha} \mu_j$$

we have

$$\begin{aligned} \frac{\partial A_{\alpha}}{\partial t} &= \sum_{j=1}^N \nu_{j\alpha} \frac{\partial \mu_j}{\partial t} \\ \Rightarrow \sum_{\alpha=1}^r J_{\alpha}^c \frac{\partial A_{\alpha}}{\partial t} &= \sum_{j=1}^N \sum_{\alpha=1}^r J_{\alpha}^c \nu_{j\alpha} \frac{\partial \mu_j}{\partial t} = \sum_{j=1}^N \frac{\partial c_j}{\partial t} \frac{\partial \mu_j}{\partial t} \end{aligned}$$

so that (12.23) becomes

$$\frac{\partial_{\chi} P}{\partial t} = -\frac{1}{T} \int dV \sum_{j=1}^N \frac{\partial c_j}{\partial t} \frac{\partial \mu_j}{\partial t} \quad (12.25)$$

Since the pressure and temperature are held constant, the chemical potentials μ_j can only be functions of the concentrations c_i . Therefore

$$\frac{\partial \mu_j}{\partial t} = \sum_{i=1}^N \left(\frac{\partial \mu_j}{\partial c_i} \right)_{PT\{c_k \neq i\}} \frac{\partial c_i}{\partial t} \quad (12.26)$$

and (12.25) becomes

$$\frac{\partial_{\chi} P}{\partial t} = -\frac{1}{T} \int dV \sum_{j=1}^N \sum_{i=1}^N \left(\frac{\partial \mu_j}{\partial c_i} \right)_{PT\{c_k \neq i\}} \frac{\partial c_i}{\partial t} \frac{\partial c_j}{\partial t} \quad (12.27a)$$

Now, as shown in section 2.H.2 and in particular eq(2.179), the matrix $\left(\frac{\partial \mu_j}{\partial c_i} \right)_{PT\{c_k \neq i\}}$

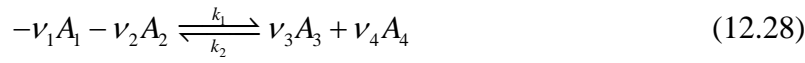
is positive semi-definite so that (12.27a) implies

$$\frac{\partial_x P}{\partial t} \leq 0 \quad (12.27)$$

Thus, condition (12.20) is indeed valid for the present case.

12.B.2.2. Stability of Nonlinear Chemical Reactions

Consider the reaction



with

$$\begin{aligned} \frac{\partial N_3}{\partial t} &= k_1 N_1^{|v_1|} N_2^{|v_2|} - k_2 N_3^{v_3} N_4^{v_4} \\ &= k_1 N_1^{|v_1|} N_2^{|v_2|} \left[1 - \frac{k_2}{k_1} \frac{N_3^{v_3} N_4^{v_4}}{N_1^{|v_1|} N_2^{|v_2|}} \right] \end{aligned} \quad (12.29)$$

Now,

$$\frac{\partial \rho_i}{\partial t} = \rho \frac{\partial c_i}{\partial t} = \bar{v}_i J = M_i \frac{\partial N_i}{\partial t}$$

where $\bar{v}_i = M_i v_i$ and N_i is the molar density, M_i the molecular weight, and $\rho_i = M_i N_i$ is the mass density.

For a system of ideal gases,

$$\begin{aligned} A &= RT \left[F(T, P) + \ln \frac{N_3^{v_3} N_4^{v_4}}{N_1^{|v_1|} N_2^{|v_2|}} \right] \\ &= RT \ln \left[K(T, P) \frac{N_3^{v_3} N_4^{v_4}}{N_1^{|v_1|} N_2^{|v_2|}} \right] \end{aligned} \quad (12.30)$$

where $K(T, P) = \exp[F(T, P)]$ and $F(T, P) = \sum_{i=1}^4 v_i \phi_i + \ln P^{\sum_i v_i}$ is independent of N_i . At equilibrium,

$$A = 0 \quad \text{and} \quad \frac{\partial N_i}{\partial t} = 0$$

\Rightarrow

$$K(T, P) \frac{N_3^{v_3} N_4^{v_4}}{N_1^{|v_1|} N_2^{|v_2|}} = 1 \quad \text{and} \quad 1 - \frac{k_2}{k_1} \frac{N_3^{v_3} N_4^{v_4}}{N_1^{|v_1|} N_2^{|v_2|}} = 0$$

which means

$$K(T, P) = \frac{k_2}{k_1}$$

Hence,

$$\begin{aligned}
\frac{\partial N_3}{\partial t} &= \frac{\bar{V}_3}{M_3} J = \nu_3 J \\
&= k_1 N_1^{|\nu_1|} N_2^{|\nu_2|} \left[1 - K(T, P) \frac{N_3^{\nu_3} N_4^{\nu_4}}{N_1^{|\nu_1|} N_2^{|\nu_2|}} \right] \\
&= k_1 N_1^{|\nu_1|} N_2^{|\nu_2|} \left[1 - \exp\left(\frac{A}{k_B T}\right) \right]
\end{aligned} \tag{12.31}$$

thus relating the reaction rate J to the affinity A . For small A , we have

$$J \simeq -\frac{k_1}{\nu_3} N_1^{|\nu_1|} N_2^{|\nu_2|} \frac{A}{k_B T}$$

Now, for constant T and P , we have

$$\begin{aligned}
\Delta S &= -\frac{1}{2T} \sum_{i,j=1}^n \left(\frac{\partial \mu'_i}{\partial N_j} \right)_{PTN_{k \neq j}} \Delta N_i \Delta N_j \\
&= -\frac{1}{2T} \sum_{i,j=1}^n \left(\frac{\partial \mu_i}{\partial n_j} \right)_{PTn_{k \neq j}} \Delta n_i \Delta n_j
\end{aligned}$$

Using

$$n_i = \frac{\rho_i V}{M_i} = \frac{c_i}{M_i} \rho V \quad [M_i \text{ is the molar weight }]$$

we have

$$\frac{\Delta S}{V} = -\frac{1}{2T} \sum_{i,j=1}^n \left(\frac{\partial \mu_i}{\partial c_j} \right)_{PTc_{k \neq j}} \Delta c_i \Delta c_j \frac{\rho}{M_i}$$

Stability of Steady State of Purely Chemical Reactions

Near equilibrium, we have

$$S_{local} = S_{local}^0 + \delta S_{local} + \frac{1}{2} \delta^2 S_{local} + \dots \tag{12.32}$$

with

$$\frac{1}{2V} \delta^2 S_{local} = -\frac{\rho}{2T} \sum_{i,j=1}^n \left(\frac{\partial \mu_i}{\partial c_j} \right)_{PTc_{k \neq j}}^0 \Delta c_i \Delta c_j \frac{1}{M_i} \leq 0 \tag{12.33}$$

where the inequality results from the fact that the matrix $\left(\frac{\partial \mu_i}{\partial c_j} \right)_{PTc_{k \neq j}}^0$ is non-negative.

Now,

$$\frac{\partial c_i}{\partial t} = \frac{1}{\rho} \sum_{k=1}^r \bar{v}_i^k J_k$$

$$\Rightarrow \frac{\partial \delta c_i}{\partial t} = \frac{1}{\rho} \sum_{k=1}^r \bar{v}_i^k \delta J_k$$

Also,

$$\delta \mu_i = \sum_{j=1}^n \left(\frac{\partial \mu_i}{\partial c_j} \right)_{PTc_{k \neq j}} \delta c_j$$

Hence, using

$$A_k = \sum_{j=1}^n v_j^k \mu_j$$

we have

$$\delta A_k = \sum_{j=1}^n v_j^k \delta \mu_j = \sum_{i,j=1}^n v_j^k \left(\frac{\partial \mu_j}{\partial c_i} \right)_{PTc_{k \neq i}} \delta c_i$$

Consider now,

$$\frac{1}{2V} \frac{\partial}{\partial t} \delta^2 S_{local} = -\frac{\rho}{2T} \sum_{i,j=1}^n \left(\frac{\partial \mu_i}{\partial c_j} \right)_{PTc_{k \neq j}}^0 \left[\frac{\partial \delta c_i}{\partial t} \delta c_j + \delta c_i \frac{\partial \delta c_j}{\partial t} \right] \frac{1}{M_i}$$

Since,

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{TPn_{j \neq i}} = \frac{1}{n} \left(\frac{\partial G}{\partial c_i} \right)_{TPc_{j \neq i}}$$

we have

$$\left(\frac{\partial \mu_i}{\partial c_j} \right)_{TPc_{k \neq j}} = \frac{1}{n} \left(\frac{\partial^2 G}{\partial c_j \partial c_i} \right)_{TPc_{k \neq j \neq i}}$$

$$\left(\frac{\partial \mu_j}{\partial c_i} \right)_{TPc_{k \neq i}} = \frac{1}{n} \left(\frac{\partial^2 G}{\partial c_i \partial c_j} \right)_{TPc_{k \neq j \neq i}}$$

$$\Rightarrow \left(\frac{\partial \mu_i}{\partial c_j} \right)_{TPc_{k \neq j}} = \left(\frac{\partial \mu_j}{\partial c_i} \right)_{TPc_{k \neq i}}$$

Therefore,

$$\frac{1}{2V} \frac{\partial}{\partial t} \delta^2 S_{local} = -\frac{\rho}{T} \sum_{i,j=1}^n \left(\frac{\partial \mu_i}{\partial c_j} \right)_{PTc_{k \neq j}}^0 \delta c_j \frac{\partial \delta c_i}{\partial t} \frac{1}{M_i}$$

$$\begin{aligned}
&= -\frac{\rho}{T} \sum_{i,j=1}^n \left(\frac{\partial \mu_i}{\partial c_j} \right)_{PTc_{k \neq j}}^0 \delta c_j \frac{1}{\rho} \sum_{k=1}^r \nu_i^k \delta J_k \\
&= -\frac{1}{T} \sum_{k=1}^r \delta A_k \delta J_k
\end{aligned}$$

so that

$$\begin{aligned}
\frac{\partial}{\partial t} \left(\frac{1}{2} \delta^2 S_{total} \right) &= \int dV \frac{\partial}{\partial t} \left(\frac{1}{2V} \delta^2 S_{local} \right) \\
&= -\int dV \frac{1}{T} \sum_{k=1}^r \delta A_k \delta J_k
\end{aligned}$$

Now,

$$\delta^2 S_{total} = \int dV \frac{1}{V} \delta^2 S_{local} \leq 0$$

Therefore, if $\frac{\partial}{\partial t} \delta^2 S_{total} > 0$, the steady state is stable [see Lyapounov function].

Consider the entropy production

$$P = -\int dV \frac{1}{T} \sum_{k=1}^r A_k J_k$$

\Rightarrow

$$\delta P|_{\chi} = -\int dV \frac{1}{T} \sum_{k=1}^r J_k \delta A_k$$

where $|_{\chi}$ means fixed J . In the steady state, J_k^0 corresponding to the forces A_k

that are not held fixed vanish [see Minimum Entropy Production]. Therefore,

$$J_k = \delta J_k + \frac{1}{2} \delta^2 J_k + \dots$$

so that

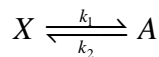
$$\delta P|_{\chi} \approx -\int dV \frac{1}{T} \sum_{k=1}^r \delta J_k \delta A_k = \frac{\partial}{\partial t} \left(\frac{1}{2} \delta^2 S_{total} \right)$$

which means for stable states,

$$\delta P|_{\chi} > 0$$

Example

Consider the unimolecular reaction



with $\nu_A = -\nu_X = 1$ and

$$\frac{dN_X}{dt} = -k_1 N_X + k_2 N_A = -\frac{dN_A}{dt}$$

In the steady state,

$$\frac{dN_X}{dt} = 0$$

so that

$$N_X^0 = \frac{k_2}{k_1} N_A$$

$$J = \frac{M_i}{\bar{v}_i} \frac{\partial N_i}{\partial t} = \frac{1}{\nu_i} \frac{\partial N_i}{\partial t} = \frac{1}{\nu_X} \frac{\partial N_X}{\partial t} = \frac{1}{\nu_A} \frac{\partial N_A}{\partial t} = k_1 N_X - k_2 N_A$$

$$A = \sum_{i=X,A} \mu_i \nu_i = RT \ln \left(\frac{k_2}{k_1} \frac{N_A}{N_X} \right)$$

In the steady state, $N_X = N_X^0$ so that $A = 0$. Hence, the steady state is also the equilibrium state. Now, let N_A be held fixed away from the equilibrium value so that

$$\delta J = k_1 \delta N_X$$

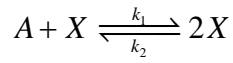
$$\delta A = -RT \frac{\delta N_X}{N_X}$$

$$\Rightarrow \delta P|_z = -\frac{1}{T} \delta A \delta J = k_1 R \frac{(\delta N_X)^2}{N_X} > 0$$

Therefore, the steady state is stable.

12.B.2.3. Exercise 12.1

Consider the auto-catalytic reaction



with

$$\frac{dN_X}{dt} = k_1 N_A N_X - k_2 N_X^2 = J$$

where the sign of the k_1 (k_2) term is + (-) since there is one more (less) X after the

\rightarrow (\leftarrow) reaction. Also, the net stoichiometric coefficient for X is $\nu_X = +1$. Thus,

$$A = RT \ln \left(\frac{k_2 N_X^2}{k_1 N_A N_X} \right) = RT \ln \left(\frac{k_2 N_X}{k_1 N_A} \right)$$

For the steady state,

$$\frac{dN_X}{dt} = 0 \quad \Rightarrow \quad \begin{cases} N_X^0 = 0 \\ N_X^0 = \frac{k_1}{k_2} N_A \end{cases}$$

The case $N_X^0 = \frac{k_1}{k_2} N_A$ also implies $A = 0$ so that it is an equilibrium state.

Now, let N_A be held fixed away from the equilibrium value so that

$$\delta J = (k_1 N_A - 2k_2 N_X^0) \delta N_X$$

$$\delta A = RT \frac{\delta N_X}{N_X^0}$$

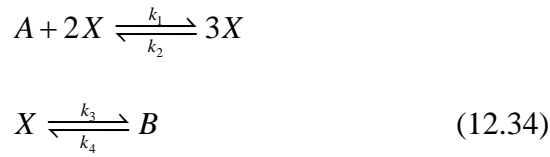
$$\Rightarrow \quad \delta P|_x = -\frac{R}{N_X^0} (k_1 N_A - 2k_2 N_X^0) (\delta N_X)^2$$

For $N_X^0 = 0$, we have $\delta P|_x \rightarrow -\infty$ so that the state is unstable.

For $N_X^0 = \frac{k_1}{k_2} N_A$, we have $\delta P|_x = -Rk_2 (\delta N_X)^2 > 0$ so that the state is stable.

12.C. The Schlogl Model

Consider the reactions



with rates

$$\frac{dN_X}{dt} = k_1 N_A N_X^2 - k_2 N_X^3 - k_3 N_X + k_4 N_B \quad (12.46)$$

$$\frac{dN_A}{dt} = -k_1 N_A N_X^2 + k_2 N_X^3$$

$$\frac{dN_B}{dt} = k_3 N_X - k_4 N_B$$

$$\frac{dN_X}{dt} = -\frac{dN_A}{dt} - \frac{dN_B}{dt}$$

currents

$$J_1 = \frac{1}{v_A} \frac{dN_A}{dt} = k_1 N_A N_X^2 - k_2 N_X^3$$

$$J_2 = \frac{1}{v_B} \frac{dN_B}{dt} = k_3 N_X - k_4 N_B$$

and affinities

$$A_1 = RT \ln \left(\frac{k_2}{k_1} \frac{N_X^3}{N_A N_X^2} \right) = RT \ln \left(\frac{k_2}{k_1} \frac{N_X}{N_A} \right)$$

$$A_2 = RT \ln \left(\frac{k_4}{k_3} \frac{N_B}{N_X} \right)$$

At equilibrium, we have $A_1 = A_2 = 0$ so that using overbars to indicate equilibrium values, we have

$$k_2 \bar{N}_X = k_1 \bar{N}_A \quad \text{and} \quad k_4 \bar{N}_B = k_3 \bar{N}_X \quad (12.44)$$

Let

$$\bar{R} = \frac{\bar{N}_A}{\bar{N}_B} = \frac{k_2 k_4}{k_1 k_3} \quad (12.45)$$

At a steady state with

$$\frac{dN_X}{dt} = 0 \quad \Rightarrow \quad \frac{dN_A}{dt} + \frac{dN_B}{dt} = 0$$

we have

$$\begin{aligned} k_1 N_A N_X^{02} - k_2 N_X^{03} - k_3 N_X^0 + k_4 N_B &= 0 \\ \Rightarrow \quad N_X^{03} - \frac{k_1 N_A}{k_2} N_X^{02} + \frac{k_3}{k_2} N_X^0 - \frac{k_4}{k_2} N_B &= 0 \\ N_X^{03} - a N_X^{02} + k N_X^0 - b &= 0 \end{aligned} \quad (12.47)$$

where

$$a = \frac{k_1 N_A}{k_2} \quad b = \frac{k_4}{k_2} N_B \quad k = \frac{k_3}{k_2}$$

For fixed a and k , b is a cubic function of N_X^0 , i.e.,

$$b = N_X^{03} - a N_X^{02} + k N_X^0$$

The extrema of b are given by

$$\frac{db}{dN_X^0} = 3N_X^{02} - 2a N_X^0 + k = 0 \quad (12.48)$$

with solutions

$$N_X^\pm = \frac{1}{3} \left(a \pm \sqrt{a^2 - 3k} \right) \quad (12.49)$$

so that

$$b^\pm = b(N_X^\pm) = (N_X^\pm)^3 - a(N_X^\pm)^2 + k N_X^\pm$$

Now,

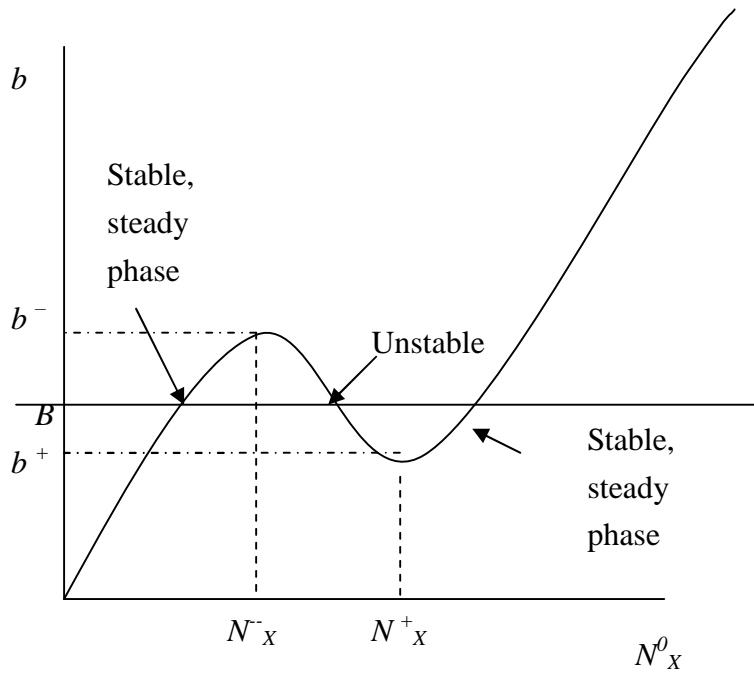
$$\frac{d^2 b}{dN_X^{02}} = 6N_X^0 - 2a \begin{pmatrix} > 0 \\ = 0 \\ < 0 \end{pmatrix} \quad \text{for} \quad N_X^0 \begin{pmatrix} > \\ = \\ < \end{pmatrix} \frac{a}{3}$$

Also,

$$b \rightarrow \infty \quad \text{as} \quad N_X^0 \rightarrow \infty$$

$$b = 0 \quad \text{as} \quad N_X^0 = 0$$

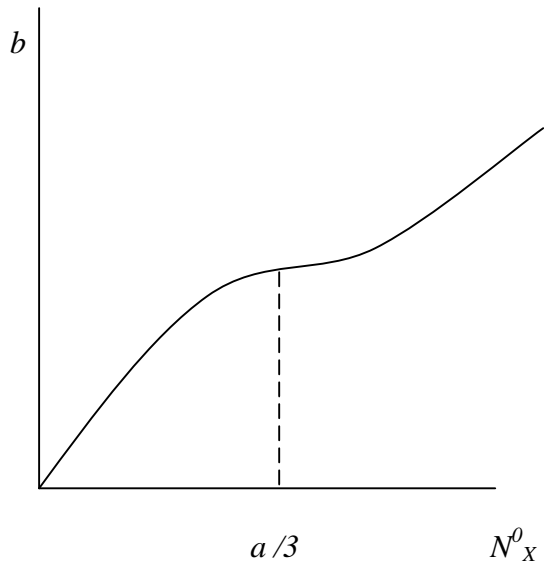
Thus, assuming $a^2 > 3k$ so that N_X^\pm are real, the graph of $b = b(N_X^0)$ is



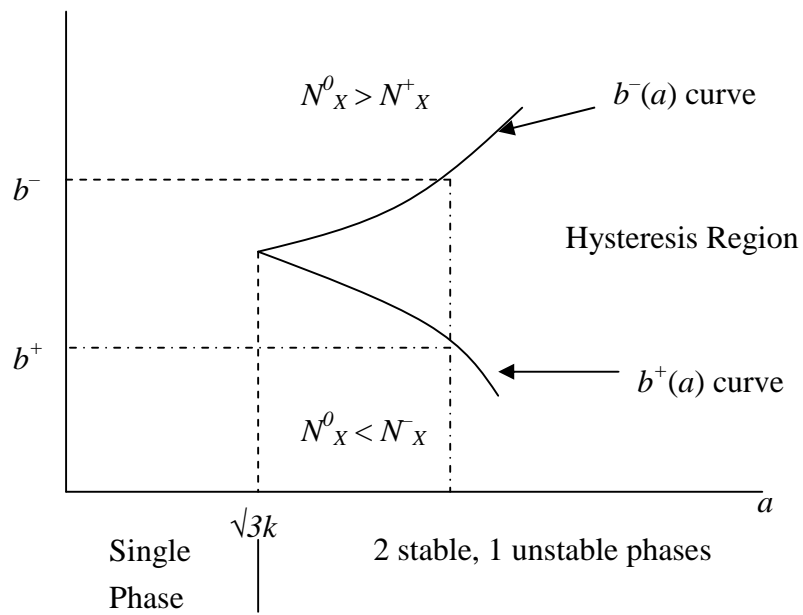
Therefore, there are 3 phases as indicated by the intersects of the line B with the curve.

Of these, the one with $N_x^- < N_x^0 < N_x^+$ is unstable.

For $a^2 \leq 3k$, there is no extrema so that there is only an inflection point at $N_x^0 = \frac{a}{3}$



Thus, the phase diagram in the $b - a$ plane is



12.D. The Brusselator

- 12.D.1. [The Brusselator – A NonLinear Chemical Model](#)
- 12.D.2. [Boundary Conditions](#)
- 12.D.3. [Linear Stability Analysis](#)

12.D.1. The Brusselator – A NonLinear Chemical Model

Belousov- Zhabotinski reaction

Ce ion catalyzed oxidation of Molonic acid by Bromate in Sulfuric acid medium:

1. Well-stirred:

Periodic changes of Br^- , Ce^{4+} / Ce^{3+} concentrations (spatially homogeneous) \Rightarrow color changes (chemical clock)

2. Unstirred, shallow dish:

Travelling waves of Br^- , Ce^{4+} / Ce^{3+} concentrations.

See R.J.Field, R.M.Noyes, J.Chem.Phys. 60, 1877 (74).

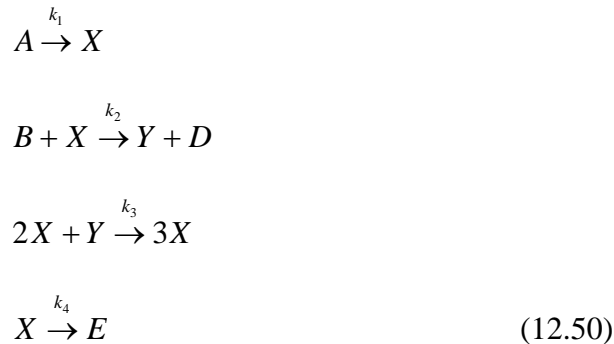
3 Variable Intermediates Model (Oregonator)

See R.J.Field, J.Chem.Phys. 63, 2289 (75).

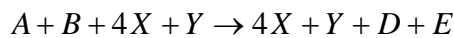
Simplified Model (Brusselator)

See I.Prigogine, Lefever, J.Chem.Phys. 48, 1695 (68).

The **Brusselator** consists of 4 reactions involving 6-components:



Adding these reactions gives



or $A + B \rightarrow D + E$ (net reaction)

Thus, X and Y are catalysis. Furthermore, the k_3 reaction shows that X is autocatalytic (it appears on both sides of the reaction) and provides the non-linearity.

In a typical run, A , B are kept in excess while D , E are removed instantly so that concentrations of A , B , D and E are fixed. Thus, the affinity A is large and the system is far from chemical equilibrium. X , Y then exhibit variations in time / space.

Rate Equations

The rate equations are

$$\frac{\partial N_X}{\partial t'} = D'_X \nabla^2 N_X + k_1 N_A - k_2 N_B N_X + k_3 N_X^2 N_Y - k_4 N_X \quad (12.51)$$

$$\frac{\partial N_Y}{\partial t'} = D'_Y \nabla^2 N_Y + k_2 N_B N_X - k_3 N_X^2 N_Y \quad (12.52)$$

where D'_X and D'_Y are diffusion co-efficients. Note that the k_2 and k_3 reactions contribute equal amounts but with opposite signs to $\frac{\partial N_X}{\partial t'}$ and $\frac{\partial N_Y}{\partial t'}$.

In order to simplify the notations, we would like to absorb the k 's into the N 's and write (1) as

$$\frac{\partial X}{\partial t} = D_X \nabla^2 X + A - BX + X^2 Y - X \quad (12.53)$$

$$\frac{\partial Y}{\partial t} = D_Y \nabla^2 Y + BX - X^2 Y \quad (12.54)$$

To this end, we set

$$X = \alpha_X N_X \quad t = \alpha_t t' \quad \text{etc}$$

so that 7 α 's for $X, Y, A, B, t, D_X,$ and D_Y . Eq(12.53-4) then become

$$\frac{\alpha_X}{\alpha_t} \frac{\partial N_X}{\partial t'} = \alpha_{D_X} \alpha_X D'_X \nabla^2 N_X + \alpha_A N_A - \alpha_B \alpha_X N_B N_X + \alpha_X^2 \alpha_Y N_X^2 N_Y - \alpha_X N_X$$

$$\frac{\alpha_Y}{\alpha_t} \frac{\partial N_Y}{\partial t'} = \alpha_{D_Y} \alpha_Y D'_Y \nabla^2 N_Y + \alpha_B \alpha_X N_B N_X - \alpha_X^2 \alpha_Y N_X^2 N_Y$$

Rearranging, we have

$$\frac{\partial N_X}{\partial t'} = \alpha_{D_X} \alpha_t D'_X \nabla^2 N_X + \frac{\alpha_A \alpha_t}{\alpha_X} N_A - \alpha_B \alpha_t N_B N_X + \alpha_X \alpha_Y \alpha_t N_X^2 N_Y - \alpha_t N_X$$

$$\frac{\partial N_Y}{\partial t'} = \alpha_{D_Y} \alpha_t D'_Y \nabla^2 N_Y + \frac{\alpha_B \alpha_X \alpha_t}{\alpha_Y} N_B N_X - \alpha_X^2 \alpha_t N_X^2 N_Y$$

Comparing with (12.51-2) gives

$$\alpha_{D_X} \alpha_t = 1$$

$$\alpha_{D_Y} \alpha_t = 1$$

$$\frac{\alpha_A \alpha_t}{\alpha_X} = k_1$$

$$\frac{\alpha_B \alpha_X \alpha_t}{\alpha_Y} = k_2$$

$$\alpha_B \alpha_t = k_2$$

$$\alpha_X^2 \alpha_t = k_3$$

$$\alpha_X \alpha_Y \alpha_t = k_3$$

$$\alpha_t = k_4$$

Thus, there are 8 equations for 7 variables. However, the 4 equations involving k_2 and k_3 are not independent. They reduce to 2 equations by setting $\alpha_X = \alpha_Y$. Thus, we have

$$\alpha_t = k_4$$

$$\alpha_{D_x} = \frac{1}{\alpha_t} = \frac{1}{k_4} \qquad \alpha_{D_y} = \frac{1}{\alpha_t} = \frac{1}{k_4}$$

$$\alpha_B = \frac{k_2}{\alpha_t} = \frac{k_2}{k_4}$$

$$\alpha_X^2 = \frac{k_3}{\alpha_t} = \frac{k_3}{k_4} \quad \Rightarrow \quad \alpha_X = \sqrt{\frac{k_3}{k_4}} = \alpha_Y$$

$$\alpha_A = \frac{\alpha_X k_1}{\alpha_t} = \sqrt{\frac{k_3}{k_4}} \frac{k_1}{k_4} = \sqrt{\frac{k_3 k_1^2}{k_4^3}}$$

i.e.,

$$t = k_4 t'$$

$$D_X = \frac{D'_X}{k_4} \qquad D_Y = \frac{D'_Y}{k_4}$$

$$B = \frac{k_2}{k_4} N_B \qquad A = \sqrt{\frac{k_3 k_1^2}{k_4^3}} N_A$$

$$X = \sqrt{\frac{k_3}{k_4}} N_X \qquad Y = \sqrt{\frac{k_3}{k_4}} N_Y$$

Steady Uniform State

For a steady state

$$\frac{\partial X}{\partial t} = \frac{\partial Y}{\partial t} = 0$$

For a uniform state

$$\nabla^2 X = \nabla^2 Y = 0$$

Hence, for a steady, uniform state, eq(2) becomes

$$A - (B+1)X + X^2 Y = 0$$

$$BX - X^2 Y = 0$$

The 2nd equation gives

$$X = 0 \qquad \text{or} \qquad X = \frac{B}{Y}$$

Now, the $X = 0$ solution can be discarded since it means nothing happens.

For the $X = \frac{B}{Y}$ solution, the 1st equation becomes

$$A - \frac{B(B+1)}{Y} + \frac{B^2}{Y} = 0$$

$$\Rightarrow Y_0 = \frac{B_0}{A_0} \quad \text{and} \quad X_0 = A_0 \quad (12.55)$$

where we've used the subscript 0 to indicate the steady, uniform state. In terms of the usual parameters, we have

$$X_0 = A_0 \Rightarrow \sqrt{\frac{k_3}{k_4}} N_X^0 = \sqrt{\frac{k_3 k_1^2}{k_4^3}} N_A^0 \Rightarrow N_X^0 = \frac{k_1}{k_4} N_A^0$$

$$Y_0 = \frac{B_0}{A_0} \Rightarrow \sqrt{\frac{k_3}{k_4}} N_Y^0 = \frac{k_2}{k_4} \sqrt{\frac{k_4^3}{k_3 k_1^2}} \frac{N_B^0}{N_A^0} \Rightarrow N_Y^0 = \frac{k_2 k_4}{k_3 k_1} \frac{N_B^0}{N_A^0}$$

Reverse Reactions

Now, if the reverse reactions are allowed with reaction constants k'_i , we have

$$\frac{\partial N_X}{\partial t'} = D'_X \nabla^2 N_X + k_1 N_A - k_2 N_B N_X + k_3 N_X^2 N_Y - k_4 N_X$$

$$k'_1 N_X + k'_2 N_Y N_D - k'_3 N_X^3 + k'_4 N_E$$

and similarly for N_Y , N_A , ..., etc. In chemical equilibrium, the k_i and k'_i reactions cancel pairwise, e.g., $k_4 N_X = k'_4 N_E$, ..., etc. Hence, the N_X^0 and N_Y^0 solutions

are also solutions of the chemical equilibrium (with appropriate N_E^0 and N_D^0). In other words, the steady, uniform states are on the thermodynamics branch.

Stability

To study the stability of the steady, uniform state, we set

$$\alpha = X - X_0 = X - A \quad (12.56)$$

$$\beta = Y - Y_0 = Y - \frac{B}{A} \quad (12.57)$$

Eq(2) then becomes

$$\frac{\partial \alpha}{\partial t} = D_X \nabla^2 \alpha + A - B(\alpha + A) + (\alpha + A)^2 \left(\beta + \frac{B}{A} \right) - (\alpha + A)$$

$$\frac{\partial \beta}{\partial t} = D_Y \nabla^2 \beta + B(\alpha + A) - (\alpha + A)^2 \left(\beta + \frac{B}{A} \right)$$

Keeping only terms linear in α and β , we have

$$\frac{\partial \alpha}{\partial t} \simeq D_x \nabla^2 \alpha + A - B\alpha - BA + 2\alpha B + A^2 \beta + AB - \alpha - A$$

$$= D_x \nabla^2 \alpha + (B-1)\alpha + A^2 \beta$$

$$\frac{\partial \beta}{\partial t} \simeq D_y \nabla^2 \beta + B\alpha + BA - 2B\alpha - A^2 \beta - AB$$

$$= D_y \nabla^2 \beta - B\alpha - A^2 \beta$$

Rearranging, we have

$$\frac{\partial \alpha}{\partial t} = [D_x \nabla^2 + (B-1)]\alpha + A^2 \beta \quad (12.58)$$

$$\frac{\partial \beta}{\partial t} = (D_y \nabla^2 - A^2)\beta - B\alpha \quad (12.59)$$

Note that these equations govern the kinetics of the system near $\alpha = \beta = 0$, the steady, homogeneous, state. Since these equations are linear,

1. Different components of the Fourier transform of α and β don't mix.
2. Study of 1 component (\mathbf{k}, ω) is enough.

12.D.2. Boundary Conditions

Particular solutions require the specification of boundary conditions. We'll assume the system to be contained in a box of sides L and set

$$\mathbf{k} = \sum_{i=x,y,z} \frac{n_i \pi}{L} \hat{\mathbf{e}}_i$$

Case I: Dirichlet Boundary Conditions

$X = X_0$ and $Y = Y_0$ on boundary.

$\Rightarrow \alpha = \beta = 0$ on boundary.

$$\therefore \alpha(\mathbf{r}, t) = \tilde{\alpha}(\mathbf{k}, \omega) \sin k_x x \sin k_y y \sin k_z z e^{\omega t} \quad (12.60)$$

$$\beta(\mathbf{r}, t) = \tilde{\beta}(\mathbf{k}, \omega) \sin k_x x \sin k_y y \sin k_z z e^{\omega t} \quad (12.61)$$

Case II: Neumann Boundary Conditions

$\hat{\mathbf{n}} \cdot \nabla X = \hat{\mathbf{n}} \cdot \nabla Y = 0$ on boundary. ($\hat{\mathbf{n}} \perp \text{surface}$)

$\Rightarrow \hat{\mathbf{n}} \cdot \nabla \alpha = \hat{\mathbf{n}} \cdot \nabla \beta = 0$ on boundary.

$$\therefore \alpha(\mathbf{r}, t) = \tilde{\alpha}(\mathbf{k}, \omega) \cos k_x x \cos k_y y \cos k_z z e^{\omega t} \quad (12.62)$$

$$\beta(\mathbf{r}, t) = \tilde{\beta}(\mathbf{k}, \omega) \cos k_x x \cos k_y y \cos k_z z e^{\omega t} \quad (12.63)$$

In both cases, we have

$$\nabla^2 \alpha = -k^2 \alpha$$

$$\frac{\partial \alpha}{\partial t} = \omega \alpha$$

and similarly for β . Here,

$$k^2 = k_x^2 + k_y^2 + k_z^2 = \left(\frac{\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2) = \left(\frac{\pi}{L}\right)^2 m$$

where m is an integer. Note that

$$m = 0 \quad \Leftrightarrow \quad n_x = n_y = n_z = 0$$

Hence, $m = 0$ is not allowed for case *I* since it would imply $\alpha = \beta = 0$ identically.

However, $m = 0$ is not allowed for case *II*.

Since the time dependence of α and β are $e^{\omega t}$, we have

1. ω real

- (a) $\omega < 0$
 $\alpha \rightarrow 0$ for t large, i.e., the system return to the spatially homogeneous steady state.
- (b) $\omega > 0$
 α grows as t grows. The linearized equations will become invalid so that the state is unstable. It bifurcates to another state, thus inducing a phase transition. The new state obeys a set of non-linear equations and hence cannot be discussed using our linearized analysis. However, the condition $\omega > 0$ does indicate the on-set of the bifurcation. Finally, the new state is expected to exhibit spatial oscillations.

2. ω complex

Let $\omega = \omega_r + i\omega_i$. Time oscillation is then denoted by ω_i .

- (a) $\omega_r < 0$.

The system gradually returns to the steady state.

- (b) $\omega_r > 0$.

Bifurcate to new state, possibly oscillatory in both time and space.

(chemical clock, travelling waves, etc.)

Fourier Components

In terms of $\tilde{\alpha}$ and $\tilde{\beta}$, we have

$$\omega\tilde{\alpha} = (B - 1 - D_x k^2)\tilde{\alpha} + A^2\tilde{\beta}$$

$$\omega\tilde{\beta} = -B\tilde{\alpha} + (-A^2 - D_y k^2)\tilde{\beta}$$

or

$$\begin{pmatrix} B - 1 - D_x k^2 - \omega & A^2 \\ -B & -A^2 - D_y k^2 - \omega \end{pmatrix} \begin{pmatrix} \tilde{\alpha} \\ \tilde{\beta} \end{pmatrix} = 0 \quad (12.64)$$

i.e.,

$$\begin{pmatrix} c_1 - \omega & A^2 \\ -B & -c_2 - \omega \end{pmatrix} \begin{pmatrix} \tilde{\alpha} \\ \tilde{\beta} \end{pmatrix} = 0$$

where

$$c_1 = B - 1 - D_x k^2 \quad \text{and} \quad c_2 = A^2 + D_y k^2$$

\Rightarrow

$$\omega^2 - (c_1 - c_2)\omega - c_1 c_2 + A^2 B = 0 \quad (12.65)$$

with solutions

$$\begin{aligned}\omega_{\pm} &= \frac{1}{2} \left[c_1 - c_2 \pm \sqrt{(c_1 - c_2)^2 + 4(c_1 c_2 - A^2 B)} \right] \\ &= \frac{1}{2} \left[c_1 - c_2 \pm \sqrt{(c_1 + c_2)^2 - 4A^2 B} \right]\end{aligned}\tag{12.67}$$

12.D.3. Linear Stability Analysis

12.D.3.0. [General Discussion](#)

12.D.3.1. [Real Frequency Dispersion](#)

12.D.3.2. [Complex Frequency Dispersion](#)

12.D.3.0. General Discussion

12.D.3.1. Real Frequency Dispersion

$$(c_1 + c_2)^2 > 4A^2B \quad (12.68)$$

Now, consider the case $c_2 > c_1$ so that $\omega_- < 0$ and $\omega_+ > 0$ iff

$$(c_1 - c_2)^2 < (c_1 + c_2)^2 - 4A^2B$$

or
$$c_1c_2 - A^2B > 0 \quad (12.69)$$

\Rightarrow

$$(B - 1 - D_x k^2)(A^2 + D_y k^2) - A^2B > 0$$

$$BA^2 - A^2 + BD_y k^2 - D_y k^2 - A^2 D_x k^2 - D_x D_y k^4 - A^2 B > 0$$

$$\begin{aligned} B &> 1 + A^2 \frac{D_x}{D_y} + \frac{A^2}{D_y k^2} + D_x k^2 \\ &= 1 + A^2 \frac{D_x}{D_y} + \frac{A^2 L^2}{D_y m \pi^2} + D_x \frac{m \pi^2}{L^2} = B_m \end{aligned} \quad (12.70)$$

where $m = n_x^2 + n_y^2 + n_z^2$. Writing

$$B_m = \alpha + \frac{\beta}{m} + \gamma m$$

$$\frac{dB_m}{dm} = -\frac{\beta}{m^2} + \gamma \stackrel{Set}{=} 0$$

\Rightarrow extremum at

$$m_0 = \sqrt{\frac{\beta}{\gamma}} = \sqrt{\frac{A^2 L^2 L^2}{D_y \pi^2 D_x \pi^2}} = \frac{AL^2}{\pi^2 \sqrt{D_x D_y}}$$

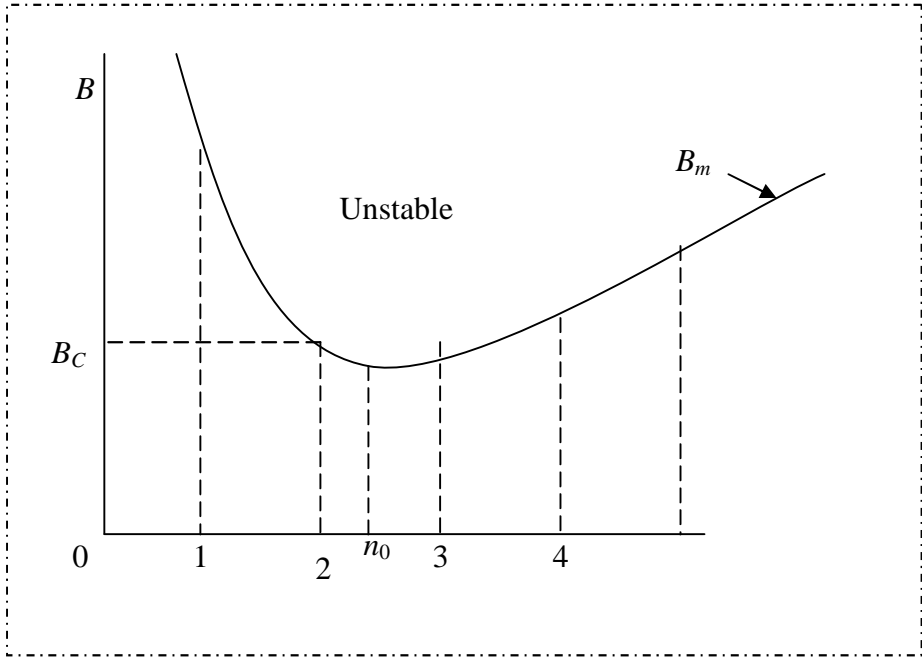
Since $B \rightarrow \infty$ for $m \rightarrow 0$ or ∞ , m_0 is a minimum.

Consider the case of a 1-dim system. We have $m = n^2$ so that

$$n_0 = \sqrt{m_0} = \sqrt{\frac{A}{\sqrt{D_x D_y}} \frac{L}{\pi}} \quad \text{is not an integer.}$$

Note that only $n = \text{integer}$ are solutions to the kinetic equation. Thus, for $B > B_c$

(the $n = 2$ line), bifurcation occurs.



12.D.3.2. Complex Frequency Dispersion

$$(c_1 + c_2)^2 < 4A^2B \quad (12.71)$$

Since everything is positive, we can write

$$c_1 + c_2 < 2A\sqrt{B}$$

or

$$B - 1 + A^2 + (D_y - D_x)k^2 < 2A\sqrt{B}$$

$$(\sqrt{B} - A)^2 - 1 + (D_y - D_x)k^2 < 0$$

$$(\sqrt{B} - A)^2 + (D_y - D_x)k^2 < 1$$

Since

$$(\sqrt{B} - A)^2 > 0$$

we have

$$(D_y - D_x)k^2 < 1 \quad \text{or} \quad D_y - D_x < \frac{L^2}{m\pi^2} \quad (12.72)$$

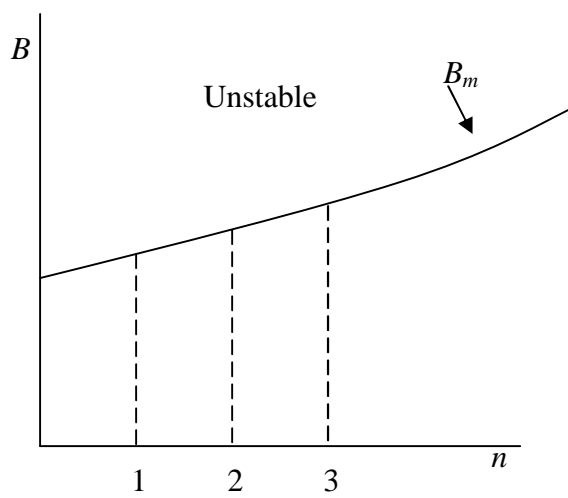
The real part of ω_{\pm} is $\frac{1}{2}(c_1 - c_2)$. Therefore, $\omega_{\pm} > 0$ if $c_1 > c_2$, i.e.,

$$B - 1 - D_x k^2 > A^2 + D_y k^2$$

$$\text{or} \quad B > 1 + A^2 + (D_x + D_y)k^2$$

$$= 1 + A^2 + (D_x + D_y) \frac{m\pi^2}{L^2} = B_m \quad (12.73)$$

Note that for case II of the Neumann B.C., $n = 0$ is allowable, which gives rise to a homogeneous time clock. Else, we have travelling waves.



12.E. The Rayleigh- Benard Instability

12.E.1. [Hydrodynamic Equations And Boundary Conditions](#)

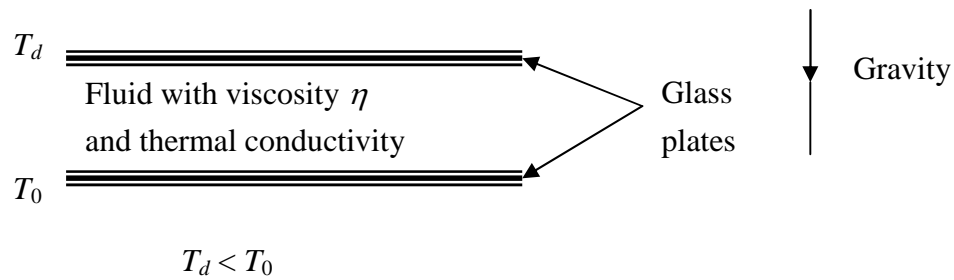
12.E.2. [Linear Stability Analysis](#)

12.E.1. Hydrodynamic Equations And Boundary Conditions

Fluid flow in pipe:

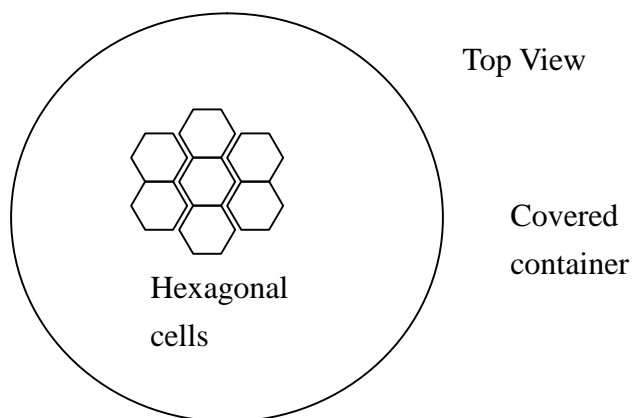
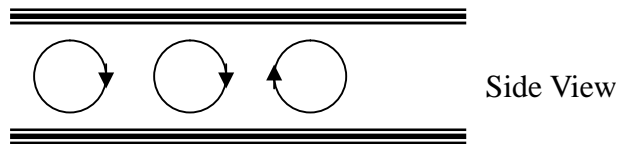
1. low velocity, high viscosity \Rightarrow smooth, steady.
2. high velocity, low viscosity \Rightarrow turbulence.

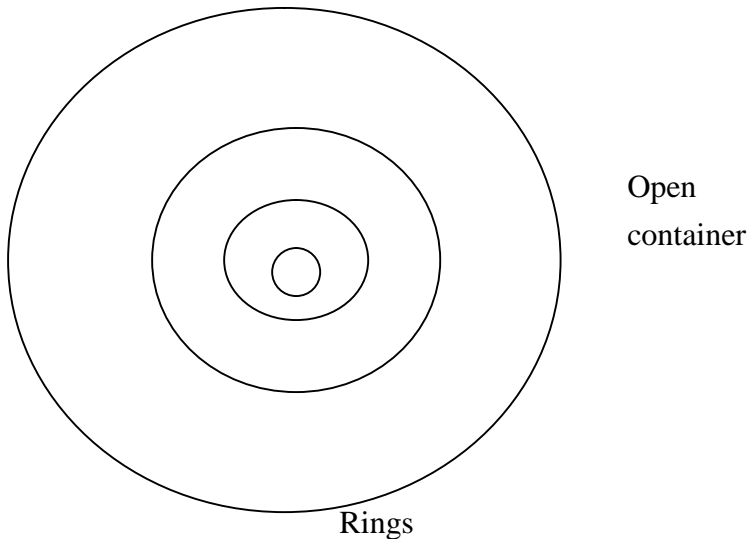
Benard's problem: (sometimes called Rayleigh-Benard problem)



For small $\Delta T = T_0 - T_d$, fluid is at rest.

For large enough ΔT , Benard's instability set in and convective flow cells appear.





Consider the Navier-Stokes equations

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \quad (\text{conservation of mass}) \quad (12.75)$$

$$\frac{\partial \rho \mathbf{v}}{\partial t} + \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = -\nabla P + \rho \mathbf{F} + \eta \nabla^2 \mathbf{v} + \left(\zeta + \frac{1}{3} \eta \right) \nabla (\nabla \cdot \mathbf{v})$$

(conservation of momentum) (12.76)

$$\frac{\partial \rho u}{\partial t} + \nabla \cdot (\rho u \mathbf{v} - K \nabla T) = \rho \dot{q} : \nabla \quad (\text{conservation of energy}) \quad (12.77)$$

For a thin fluid layer occupying the entire x - y plane,

$$\begin{aligned} \rho &\approx \rho_0 + \left. \left(\frac{\partial \rho}{\partial T} \right)_P \right|_{\rho=\rho_0} (T - T_0) \\ &= \rho_0 - \rho_0 \alpha_p (T - T_0) \end{aligned} \quad (12.78)$$

where the thermal expansivity

$$\alpha_p = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P$$

is evaluated at $\rho = \rho_0$. Rearranging, we have

$$\rho = \rho_0 [1 + \alpha_p (T_0 - T)] = \rho(z)$$

Steady State, No Flow ($\mathbf{v} = \mathbf{0}$)

The Navier-Stokes equations become

$$0 = -\nabla P + \rho \mathbf{F} = -\nabla P - \rho g \hat{\mathbf{z}} \quad (12.80)$$

$$-K \nabla^2 T = 0 \quad (12.81)$$

where $\mathbf{F} = -g \hat{\mathbf{z}}$ and g is the gravitational acceleration. Since the only variations are in the z -direction, we have

$$\frac{dP}{dz} = -\rho g = -\rho_0 [1 + \alpha_p (T_0 - T)] g$$

$$\frac{d^2 T}{dz^2} = 0$$

Using \bar{x} to denote the steady state value of x , the 2nd equation gives

$$\bar{T}(z) = c + c'z \quad (c, c' \text{ are constants})$$

With the boundary conditions

$$\bar{T}(0) = T_0 \quad \text{and} \quad \bar{T}(d) = T_d$$

we have

$$\bar{T}(z) = T_0 + \frac{T_d - T_0}{d} z \quad (12.82)$$

Hence,

$$\frac{dP}{dz} = -\rho_0 \left(1 - \alpha_p \frac{T_d - T_0}{d} z \right) g$$

with solution

$$\bar{P}(z) = P(0) - \rho_0 \left(z - \alpha_p \frac{T_d - T_0}{2d} z^2 \right) g$$

Setting $a = \frac{T_0 - T_d}{d}$, we have,

$$\bar{T}(z) = T_0 - a z$$

$$\bar{P}(z) = P_0 - \rho_0 \left(z + \frac{1}{2} a \alpha_p z^2 \right) g \quad (12.84)$$

where $P_0 = P(0)$. Note that

$$\rho = \rho_0 [1 + \alpha_p (T_0 - T)] \quad \text{and} \quad \bar{\rho} = \rho_0 (1 + a \alpha_p z) \quad (12.83)$$

Stability

Let the deviation of X from its steady state value be

$$\delta X(\mathbf{r}, t) = X(\mathbf{r}, t) - \bar{X}(z)$$

Since $\bar{\mathbf{v}} = 0$, we have $\delta \mathbf{v}(\mathbf{r}, t) = \mathbf{v}(\mathbf{r}, t)$. For small \mathbf{v} , the energy u is mostly thermal so that we can write

$$\bar{u} \simeq c_v \bar{T} \quad \text{and} \quad \delta u \simeq c_v \delta T$$

Keeping only terms linear in δX , the Navier-Stokes equations become

$$\frac{\partial \delta \rho}{\partial t} + \nabla \cdot (\bar{\rho} \mathbf{v}) = 0 \quad (12.85)$$

$$\bar{\rho} \frac{\partial \mathbf{v}}{\partial t} = -\nabla \delta P - \delta \rho g \hat{\mathbf{z}} + \eta \nabla^2 \mathbf{v} + \left(\zeta + \frac{1}{3} \eta \right) \nabla (\nabla \cdot \mathbf{v}) \quad (12.86)$$

$$\frac{\partial}{\partial t} (\bar{u} \delta \rho + \bar{\rho} \delta u) + \nabla \cdot (\bar{\rho} \bar{u} \mathbf{v} - K \nabla \delta T) = 0 \quad (12.87)$$

where the term $\nabla \cdot \mathbf{v}$ does not contribute since \mathbf{v} is proportional to partials of \mathbf{v} .

Note that the steady state satisfies

$$\frac{\partial}{\partial t} (\bar{\rho} \bar{u}) = \nabla \cdot (K \nabla \bar{T}) = 0$$

$$\frac{\partial \bar{\rho}}{\partial t} = 0$$

$$\nabla \bar{P} + \bar{\rho} g \hat{\mathbf{z}} = 0$$

$$\nabla^2 \bar{T} = 0$$

Now, (12.87) can be written as

$$\bar{u} \frac{\partial \delta \rho}{\partial t} + \bar{\rho} \frac{\partial \delta u}{\partial t} + \bar{u} \nabla \cdot (\bar{\rho} \mathbf{v}) + \bar{\rho} \mathbf{v} \cdot \nabla \bar{u} - K \nabla^2 \delta T = 0$$

which, with the help of (12.85), gives

$$\bar{\rho} \frac{\partial \delta u}{\partial t} + \bar{\rho} \mathbf{v} \cdot \nabla \bar{u} - K \nabla^2 \delta T = 0$$

\Rightarrow

$$\bar{\rho} c_v \left(\frac{\partial \delta T}{\partial t} + \mathbf{v} \cdot \nabla \bar{T} \right) - K \nabla^2 \delta T = 0$$

$$\bar{\rho} c_v \left(\frac{\partial \delta T}{\partial t} - a v_z \right) - K \nabla^2 \delta T = 0$$

Next, we can rewrite (12.85) as

$$\frac{\partial \delta \rho}{\partial t} + \mathbf{v} \cdot \nabla \bar{\rho} + \bar{\rho} \nabla \cdot \mathbf{v} = 0$$

Since $\bar{\rho} = \rho_0 (1 + a \alpha_p z) = \bar{\rho}(z)$, we have

$$\frac{\partial \bar{\rho}}{\partial t} = \frac{dz}{dt} \cdot \frac{d\bar{\rho}}{dz} = v_z \frac{d\bar{\rho}}{dz} = \mathbf{v} \cdot \nabla \bar{\rho}$$

Thus,

$$\frac{\partial \rho}{\partial t} + \bar{\rho} \nabla \cdot \mathbf{v} = 0 \quad \text{where} \quad \rho = \bar{\rho} + \delta\rho$$

Since $\rho = \rho_0 [1 + \alpha_p (T_0 - T)]$ where $T = \bar{T} + \delta T$, we have

$$\frac{\partial \rho}{\partial t} = -\rho_0 \alpha_p \frac{\partial \delta T}{\partial t}$$

Hence,

$$\nabla \cdot \mathbf{v} = \frac{\rho_0 \alpha_p}{\bar{\rho}} \frac{\partial \delta T}{\partial t}$$

Now, $\alpha_p \approx 10^{-3} \sim 10^{-4} \ll 1$ while $\frac{\partial \delta T}{\partial t}$ is expected to be small for small δT .

Therefore,

$$\nabla \cdot \mathbf{v} \approx 0 \quad (\text{Boussineq approximation})$$

and

$$\bar{\rho} = \rho_0 (1 + a\alpha_p z) \approx \rho_0$$

The linearized N-S eqs thus reduce to

$$\nabla \cdot \mathbf{v} = 0 \quad (12.89)$$

$$\rho_0 \frac{\partial \mathbf{v}}{\partial t} = -\nabla \delta P - \delta\rho g \hat{\mathbf{z}} + \eta \nabla^2 \mathbf{v} \quad (12.90)$$

$$\frac{\partial \delta T}{\partial t} - a v_z - \frac{K}{\rho_0 c_v} \nabla^2 \delta T = 0 \quad (12.91)$$

with

$$\delta\rho = -\rho_0 \alpha_p \delta T \quad (12.88)$$

Now, $\nabla \times (12.90)$ gives

$$\rho_0 \frac{\partial}{\partial t} = -g \nabla \times (\delta\rho \hat{\mathbf{z}}) + \eta \nabla^2$$

where $\nabla \times \mathbf{v}$ is the vorticity. Setting the kinematic viscosity as $\nu = \frac{\eta}{\rho_0}$ and

using (12.88), we have

$$\frac{\partial}{\partial t} = g \alpha_p \nabla \times (\delta T \hat{\mathbf{z}}) + \nu \nabla^2 \quad (12.92)$$

Since $\nabla \times (f \hat{\mathbf{z}})$ is in the x - y plane, we have

$$\frac{\partial \omega_z}{\partial t} = \nu \nabla^2 \omega_z \quad (9)$$

Using

$$\nabla \times (\nabla \times \mathbf{v}) = \nabla \times (\nabla \cdot \mathbf{v}) - \nabla^2 \mathbf{v} = -\nabla^2 \mathbf{v}$$

where the last equality is due to $\nabla \cdot \mathbf{v} = 0$. Similarly,

$$\begin{aligned} \nabla \times [\nabla \times (\delta T \hat{\mathbf{z}})] &= \nabla [\nabla \cdot (\delta T \hat{\mathbf{z}})] - \nabla^2 (\delta T \hat{\mathbf{z}}) \\ &= \nabla \left(\frac{\partial \delta T}{\partial z} \right) - \hat{\mathbf{z}} \nabla^2 \delta T \end{aligned}$$

Thus, $\nabla \times (12.92)$ gives

$$-\nabla^2 \frac{\partial \mathbf{v}}{\partial t} = g \alpha_p \left[\nabla \left(\frac{\partial \delta T}{\partial z} \right) - \hat{\mathbf{z}} \nabla^2 \delta T \right] - \nu \nabla^4 \mathbf{v}$$

so that

$$\begin{aligned} -\nabla^2 \frac{\partial v_z}{\partial t} &= g \alpha_p \left[\frac{\partial^2 \delta T}{\partial z^2} - \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \delta T \right] - \nu \nabla^4 v_z \\ \nabla^2 \frac{\partial v_z}{\partial t} &= g \alpha_p \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \delta T + \nu \nabla^4 v_z \end{aligned} \quad (12.94)$$

Thus, the z -components of $\boldsymbol{\omega}$ and \mathbf{v} are given by eqs(9) and (12.94), respectively. The situation of interest is the transition from the steady state to the Benard instability state (see figure). The actual patterns of v_z in the x - y plane are determined by the boundary conditions.

Boundary Conditions

Since the upper and lower plates are held at fixed temperatures T_0 and T_d , we have

$$\delta T(x, y, 0; t) = \delta T(x, y, d; t) = 0 \quad \text{for all } t$$

Also, the fluid is bounded between the plates so that

$$v_z(x, y, 0; t) = v_z(x, y, d; t) = 0 \quad \text{for all } t$$

These 2 conditions are general boundary conditions valid for all types of surfaces. In addition, there will be further constraints dependent on the properties of the plates.

I. Rigid Surfaces (No Tangential Flow)

$$\mathbf{v}(x, y, 0; t) = \mathbf{v}(x, y, d; t) = 0 \quad \text{for all } t$$

Thus, on the boundaries,

$$\mathbf{v} = 0$$

$$\frac{\partial \mathbf{v}}{\partial x} = \frac{\partial \mathbf{v}}{\partial y} = 0$$

$$\omega_z = \frac{\partial v_x}{\partial y} - \frac{\partial v_y}{\partial x} = 0$$

$$\frac{\partial v_z}{\partial z} = 0 \quad [\text{since } \nabla \cdot \mathbf{v} = 0 \text{ everywhere}]$$

II. Smooth Surfaces (e.g. Free Surfaces)

This means flows in the x - y plane do not exert force in the z direction. Hence,

$$\Pi_{//z} \Big|_{\text{boundary}} = 0 \quad \text{where } // \text{ denotes components in the } x\text{-}y \text{ plane.}$$

Thus,

$$\Pi_{xz}(x, y, 0; t) = \Pi_{yz}(x, y, 0; t) = \Pi_{xz}(x, y, d; t) = \Pi_{yz}(x, y, d; t) = 0$$

Since $\nabla \mathbf{v}$ is proportional to Π , we have

$$\frac{\partial v_x}{\partial z} + \frac{\partial v_z}{\partial x} = \frac{\partial v_y}{\partial z} + \frac{\partial v_z}{\partial y} = 0 \quad \text{on boundaries}$$

Since $v_z = 0$ for all x and y on boundaries, we have

$$\frac{\partial v_x}{\partial z} = \frac{\partial v_z}{\partial x} = \frac{\partial v_y}{\partial z} = \frac{\partial v_z}{\partial y} = 0 \quad \text{for all } x \text{ and } y \text{ on boundaries}$$

Thus,

$$\frac{\partial \omega_z}{\partial z} = \frac{\partial^2 v_x}{\partial z \partial y} - \frac{\partial^2 v_y}{\partial z \partial x} = \frac{\partial}{\partial y} \left(\frac{\partial v_x}{\partial z} \right) - \frac{\partial}{\partial x} \left(\frac{\partial v_y}{\partial z} \right) = 0 \quad \text{on boundaries}$$

Also,

$$\nabla \cdot \mathbf{v} = \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} = 0$$

implies

$$\begin{aligned} \frac{\partial^2 v_z}{\partial z^2} + \frac{\partial}{\partial x} \frac{\partial v_x}{\partial z} + \frac{\partial}{\partial y} \frac{\partial v_y}{\partial z} &= 0 \\ &= \frac{\partial^2 v_z}{\partial z^2} \quad \text{on boundaries} \end{aligned}$$

12.E.2. Linear Stability Analysis

In summary, the linear stability equations are

$$\frac{\partial \delta T}{\partial t} - a v_z - \frac{K}{\rho_0 c_v} \nabla^2 \delta T = 0 \quad (6)$$

$$\frac{\partial \omega_z}{\partial t} = \nu \nabla^2 \omega_z \quad (9)$$

$$\frac{\partial}{\partial t} \nabla^2 v_z = g \alpha_p \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \delta T + \nu \nabla^4 v_z \quad (10)$$

Looking for solutions periodic in the x - y plane, we write

$$X(\mathbf{r}, t) = \tilde{X}(\mathbf{k}_{//}, \omega, z) \exp(i\mathbf{k}_{//} \cdot \mathbf{r} + \omega t)$$

where

$$\mathbf{k}_{//} = k_x \hat{\mathbf{x}} + k_y \hat{\mathbf{y}} \quad \text{and} \quad \mathbf{k}_{//} \cdot \mathbf{r} = k_x x + k_y y$$

Hence,

$$\frac{\partial X}{\partial t} = \omega X \quad \text{and} \quad \nabla^2 X = \left(\frac{\partial^2}{\partial z^2} - k_{//}^2 \right) X$$

After cancelling the common exponential factor, the stability equations become

$$\omega \delta \tilde{T} - a \tilde{v}_z - \frac{K}{\rho_0 c_v} \left(\frac{\partial^2}{\partial z^2} - k_{//}^2 \right) \delta \tilde{T} = 0 \quad (12.102)$$

$$\omega \tilde{\omega}_z = \nu \left(\frac{\partial^2}{\partial z^2} - k_{//}^2 \right) \omega_z \quad (12)$$

$$\omega \left(\frac{\partial^2}{\partial z^2} - k_{//}^2 \right) \tilde{v}_z = -g \alpha_p k_{//}^2 \delta \tilde{T} + \nu \left(\frac{\partial^2}{\partial z^2} - k_{//}^2 \right)^2 \tilde{v}_z \quad (12.103)$$

Boundary Conditions

General

$$\delta T|_B = 0 \quad \Rightarrow \quad \delta \tilde{T}(0) = \delta \tilde{T}(d) = 0$$

$$v_z|_B = 0 \quad \Rightarrow \quad \delta \tilde{v}_z(0) = \delta \tilde{v}_z(d) = 0 \quad \text{for all } \mathbf{k}_{//}, \omega$$

Rigid Surface

$$\omega_z|_B = 0 \quad \Rightarrow \quad \tilde{\omega}_z(0) = \tilde{\omega}_z(d) = 0$$

$$\frac{\partial v_z}{\partial z}|_B = 0 \quad \Rightarrow \quad \frac{\partial \tilde{v}_z}{\partial z}|_{z=0} = \frac{\partial \tilde{v}_z}{\partial z}|_{z=d} = 0 \quad \text{for all } \mathbf{k}_{//}, \omega$$

Smooth Surface

$$\frac{\partial \omega_z}{\partial z}|_B = 0 \quad \Rightarrow \quad \frac{\partial \tilde{\omega}_z}{\partial z}|_{z=0} = \frac{\partial \tilde{\omega}_z}{\partial z}|_{z=d} = 0$$

$$\frac{\partial^2 v_z}{\partial z^2}|_B = 0 \quad \Rightarrow \quad \frac{\partial^2 \tilde{v}_z}{\partial z^2}|_{z=0} = \frac{\partial^2 \tilde{v}_z}{\partial z^2}|_{z=d} = 0 \quad \text{for all } \mathbf{k}_{//}, \omega$$

Solutions

(11) gives

$$\tilde{v}_z = \frac{1}{a} \left[\omega - \frac{K}{\rho_0 c_v} \left(\frac{\partial^2}{\partial z^2} - k_{//}^2 \right) \right] \delta \tilde{T}$$

Substituting into (13)

$$\left(\frac{\partial^2}{\partial z^2} - k_{//}^2 \right) \left[\omega - \nu \left(\frac{\partial^2}{\partial z^2} - k_{//}^2 \right) \right] \tilde{v}_z + g \alpha_p k_{//}^2 \delta \tilde{T} = 0$$

gives

$$\frac{1}{a} \left(\frac{\partial^2}{\partial z^2} - k_{//}^2 \right) \left[\omega - \nu \left(\frac{\partial^2}{\partial z^2} - k_{//}^2 \right) \right] \left[\omega - \frac{K}{\rho_0 c_v} \left(\frac{\partial^2}{\partial z^2} - k_{//}^2 \right) \right] \delta \tilde{T} + g \alpha_p k_{//}^2 \delta \tilde{T} = 0$$

\Rightarrow

$$\frac{\nu K}{a \rho_0 c_v} \left(\frac{\partial^2}{\partial z^2} - k_{//}^2 \right) \left(\frac{\partial^2}{\partial z^2} - k_{//}^2 - \frac{\omega}{\nu} \right) \left(\frac{\partial^2}{\partial z^2} - k_{//}^2 - \frac{\rho_0 c_v \omega}{K} \right) \delta \tilde{T} + g \alpha_p k_{//}^2 \delta \tilde{T} = 0$$

$$\left(\frac{\partial^2}{\partial z^2} - k_{//}^2 \right) \left(\frac{\partial^2}{\partial z^2} - k_{//}^2 - \frac{\omega}{\nu} \right) \left(\frac{\partial^2}{\partial z^2} - k_{//}^2 - \frac{\rho_0 c_v \omega}{K} \right) \delta \tilde{T} = - \frac{a \rho_0 c_v g \alpha_p k_{//}^2}{\nu K} \delta \tilde{T}$$

Introducing the dimensionless variable $Z = \frac{z}{d}$, we have

$$\frac{\partial^2}{\partial z^2} = \frac{1}{d^2} \frac{\partial^2}{\partial Z^2} \quad \text{and} \quad \frac{\partial^2}{\partial z^2} - A = \frac{1}{d^2} \left(\frac{\partial^2}{\partial Z^2} - A d^2 \right)$$

Now, set

$$k_{//}^2 d^2 = \alpha^2 \quad \frac{\omega}{\nu} d^2 = s$$

$$\frac{\rho_0 c_v \omega}{K} d^2 = \frac{\rho_0 c_v \nu}{K} s = \mathcal{P}s \quad \text{where} \quad \mathcal{P} = \frac{\rho_0 c_v \nu}{K}$$

$$\frac{a \rho_0 c_v g \alpha_p k_{//}^2}{\nu K} d^6 = \frac{a \rho_0 c_v g \alpha_p}{\nu K} d^4 \alpha^2 = R \alpha^2$$

where $R = \frac{a \rho_0 c_v g \alpha_p}{\nu K} d^4$ is the **Rayleigh number**. Thus,

$$\left(\frac{\partial^2}{\partial Z^2} - \alpha^2 \right) \left(\frac{\partial^2}{\partial Z^2} - s - \alpha^2 \right) \left(\frac{\partial^2}{\partial Z^2} - \mathcal{P}s - \alpha^2 \right) \delta \tilde{T} = -R \alpha^2 \delta \tilde{T}$$

Doing the same to \tilde{v}_z gives in the same equation for \tilde{v}_z . Since the B.C. are more specific on \tilde{v}_z , we shall work on it henceforth. Following the standard technique, we set

$$G = \left(\frac{\partial^2}{\partial Z^2} - \alpha^2 \right) \tilde{v}_z$$

$$F = \left(\frac{\partial^2}{\partial Z^2} - s - \alpha^2 \right) G = \left(\frac{\partial^2}{\partial Z^2} - s - \alpha^2 \right) \left(\frac{\partial^2}{\partial Z^2} - \alpha^2 \right) \tilde{v}_z$$

so that we have

$$\left(\frac{\partial^2}{\partial Z^2} - \mathcal{P}s - \alpha^2 \right) F = -R \alpha^2 \tilde{v}_z$$

$\int_0^1 dZ F^* \times (\text{both sides})$ gives

$$\int_0^1 dZ F^* \left(\frac{\partial^2}{\partial Z^2} - \mathcal{P}s - \alpha^2 \right) F = -R \alpha^2 \int_0^1 dZ F^* \tilde{v}_z$$

Consider

$$I = \int_0^1 dZ F^* \frac{\partial^2}{\partial Z^2} F = F^* \frac{\partial F}{\partial Z} \Big|_0^1 - \int_0^1 dZ \frac{\partial F^*}{\partial Z} \cdot \frac{\partial F}{\partial Z}$$

Now, F is a sum of $\frac{\partial^n \tilde{v}_z}{\partial Z^n}$ with $n = 0, 2, 4, \dots$. Hence, $\frac{\partial F}{\partial Z}$ is a sum of $\frac{\partial^n \tilde{v}_z}{\partial Z^n}$ with $n = 1, 3, 5, \dots$. Note that

For a rigid surface, $\frac{\partial^n \tilde{v}_z}{\partial Z^n} = 0$ for all n .

For a smooth surface, $\frac{\partial^n \tilde{v}_z}{\partial Z^n} = 0$ for even n .

Therefore,

$$F^* \frac{\partial F}{\partial Z} \Big|_0^1 = 0 \quad \text{for both cases.}$$

Hence,

$$I = - \int_0^1 dZ \left| \frac{\partial F}{\partial Z} \right|^2$$

and

$$\int_0^1 dZ \left[\left| \frac{\partial F}{\partial Z} \right|^2 + (\mathcal{P}_s + \alpha^2) |F|^2 \right] = R\alpha^2 \int_0^1 dZ F^* \tilde{v}_z$$

Since

$$G^* = \left(\frac{\partial^2}{\partial Z^2} - \alpha^2 \right) \tilde{v}_z^*$$

$$F^* = \left(\frac{\partial^2}{\partial Z^2} - s^* - \alpha^2 \right) G^*$$

Thus,

$$\begin{aligned} J &= \int_0^1 dZ F^* \tilde{v}_z = \int_0^1 dZ \tilde{v}_z \left(\frac{\partial^2}{\partial Z^2} - s^* - \alpha^2 \right) G^* \\ &= \int_0^1 dZ \left(\frac{\partial^2 \tilde{v}_z}{\partial Z^2} G^* - (s^* + \alpha^2) \tilde{v}_z G^* \right) \quad \text{[integration by parts twice]} \\ &= \int_0^1 dZ \left(|G|^2 - s^* \tilde{v}_z G^* \right) \quad \left[G = \frac{\partial^2 \tilde{v}_z}{\partial Z^2} - \alpha^2 \tilde{v}_z \right] \\ &= \int_0^1 dZ \left[|G|^2 - s^* \tilde{v}_z \left(\frac{\partial^2}{\partial Z^2} - \alpha^2 \right) \tilde{v}_z^* \right] \end{aligned}$$

$$= \int_0^1 dZ \left[|G|^2 + s^* \left(\left| \frac{\partial^2 \tilde{v}_z}{\partial Z^2} \right|^2 + \alpha^2 |\tilde{v}_z|^2 \right) \right] \quad [\text{integration by parts once}]$$

Hence,

$$\int_0^1 dZ \left[\left| \frac{\partial F}{\partial Z} \right|^2 + (\mathcal{P}s + \alpha^2) |F|^2 \right] = R\alpha^2 \int_0^1 dZ \left[|G|^2 + s^* \left(\left| \frac{\partial^2 \tilde{v}_z}{\partial Z^2} \right|^2 + \alpha^2 |\tilde{v}_z|^2 \right) \right]$$

Since only s is complex, the imaginary part gives

$$\int_0^1 dZ \mathcal{P} \operatorname{Im}(s) |F|^2 = R\alpha^2 \int_0^1 dZ \left[-\operatorname{Im}(s) \left(\left| \frac{\partial^2 \tilde{v}_z}{\partial Z^2} \right|^2 + \alpha^2 |\tilde{v}_z|^2 \right) \right]$$

or

$$\operatorname{Im}(s) \int_0^1 dZ \left\{ \mathcal{P} |F|^2 + R\alpha^2 \left(\left| \frac{\partial^2 \tilde{v}_z}{\partial Z^2} \right|^2 + \alpha^2 |\tilde{v}_z|^2 \right) \right\} = 0$$

Since $\mathcal{P}, R > 0$, the integrand is always positive unless $\tilde{v}_z \equiv 0$. Thus, other than the steady state, we must have $\operatorname{Im}(s) = 0$, i.e., s is real and likewise $\omega = \frac{vS}{d^2}$. Hence,

$$s > 0 \quad \Rightarrow \quad \text{system is unstable.}$$

$$s < 0 \quad \Rightarrow \quad \text{system is stable.}$$

so that $s = 0$ is the transition point. Setting $s = 0$, we have

$$\left(\frac{\partial^2}{\partial Z^2} - \alpha^2 \right)^3 \tilde{v}_z = -R\alpha^2 \tilde{v}_z \quad [\text{eigen-equation}]$$

Note that $\alpha \propto k_{//}$ and $R \propto a \propto \Delta T$. Now, the imposition of boundary conditions will in general restrict the eigenvalues $R\alpha^2$ to discrete values. Thus, $k_{//}$ and ΔT are related. Note that the reciprocal of $k_{//}$ is proportional to the cell size.

As we increase R from 0, the system will become unstable as $R\alpha^2$ reaches the 1st eigenvalue.

If both plates are smooth boundaries,

$$\frac{\partial^{2m} \tilde{v}_z}{\partial Z^{2m}} = 0 \quad \text{at } Z = 0, 1 \text{ for all } m.$$

\Rightarrow

$$\tilde{v}_z = A \sin n\pi Z \quad n = 1, 2, \dots$$

$$\frac{\partial^2 \tilde{v}_z}{\partial Z^2} = -(n\pi)^2 \tilde{v}_z$$

so that the eigen-equation becomes

$$\left[-(n\pi)^2 - \alpha^2 \right]^3 = -R\alpha^2$$

i.e.,
$$R = \frac{\left[(n\pi)^2 + \alpha^2 \right]^3}{\alpha^2}$$

The smallest R is therefore

$$R = \frac{(\pi^2 + \alpha^2)^3}{\alpha^2}$$

This may be further reduced by adjusting α so that $\frac{dR}{d\alpha^2} = 0$. Thus,

$$\begin{aligned} \frac{dR}{d\alpha^2} &= \frac{3(\pi^2 + \alpha^2)^2}{\alpha^2} - \frac{(\pi^2 + \alpha^2)^3}{\alpha^4} \\ &= \frac{(\pi^2 + \alpha^2)^2}{\alpha^4} [3\alpha^2 - (\pi^2 + \alpha^2)] \\ &= \frac{(\pi^2 + \alpha^2)^2}{\alpha^4} (2\alpha^2 - \pi^2) = 0 \end{aligned}$$

which gives only one real α solution as

$$\alpha^2 = \frac{\pi^2}{2} \quad \Rightarrow \quad \alpha_c = \frac{\pi}{\sqrt{2}} \approx 2.22$$

and

$$\lambda_c = \frac{2\pi d}{\alpha_c} = 2\sqrt{2}d$$

$$R_c = \frac{(\pi^2 + \alpha_c^2)^3}{\alpha_c^2} = \frac{\left(\frac{3}{2}\pi^2 \right)^3}{\frac{\pi^2}{2}} = \frac{27}{4}\pi^4 \approx 657.51$$

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