

9 Chapter 9: Order and Dissipation

9.1 Introduction

Will study the emergence of order both in time and in space under the influence of dissipation. Eg. chemical oscillations (or rotations) – connected with important biological problems such as the mechanism of biological clocks.

As shown in Chpt. 8, such oscillations may only occur far from equilibrium.

In macroscopic physics we can distinguish between two types of structures:

1. equilibrium structures, eg. crystals
2. non-equilibrium (or dissipative) structures

Classical thermodynamics has resolved the problem between randomness and organization for equilibrium conditions. As the temperature is lowered the contribution of the internal energy to the Helmholtz free energy

$$F = E - TS \quad (1)$$

becomes more and more dominant.

Phase transitions (eg. liquid \rightarrow solid) are characterized by a well defined loss of entropy (or increase in organization). We have seen in situations out of equilibrium that the steady state may be characterized by a reduced entropy (see for example our evaluation of the Knudsen gas (Chpt. 7). Dissipative processes may therefore also lead to an increase in organization.

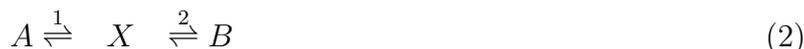
However, in the case of the Knudsen gas the entropy decrease occurs gradually with the increase in the difference of temperature between the two phases (see Prigogine (6.50)).

Are discontinuous changes in structure due to dissipative processes possible? Would correspond to non-equilibrium “analogues” of phase transitions.

In fact, it has been shown that hydrodynamic instabilities can be described in a similar way to phase transitions in equilibrium thermodynamics.

Hydrodynamic instabilities are a special case of the following more general problem.

Consider the chemical reaction considered earlier (Chpt. 8)



All equilibrium and rate constants are put equal to 1.

We introduced a parameter γ to measure the deviation of the system from equilibrium.

$$1 - \gamma \equiv B/A \quad (5)$$

where γ measures the deviation of the steady state from thermodynamic equilibrium (for which $B/A = 1$).

We assumed the following rate equation for v_1

$$v_1 = (1 + \alpha M)(A - X) \quad (6)$$

where M was acting as the catalyst. We showed that the steady state solution was

$$\begin{aligned} M = X &= \frac{1}{2\alpha}[\alpha A - 2 + [4 + 4\alpha A(1 - \gamma) + \alpha^2 A^2]^{\frac{1}{2}}] \\ &\rightarrow \frac{1}{2}(A + B) \quad \text{for } \alpha \rightarrow 0 \\ &\rightarrow A \quad \text{for } \alpha \rightarrow \infty \end{aligned} \quad (7)$$

As a special case this equation contains the equilibrium case for which $\gamma = 0$. Then we find

$$M = X = A \quad (8)$$

We may say that the “thermodynamic solution” corresponding to $\gamma = 0$ ($A = B$) may therefore be extended to all values of γ .

However, in general, if we have a more complicated set of reactions, there may be different time-independent solutions of the equations, eg. $X_1 \dots X_n$. One of them, say X_1 contains as a special case the correct equilibrium solution corresponding to a minimum of the free energy. But, will it be the correct solution for all values of the relevant constraints, such as the affinities of the overall reactions?

What we have to require of the correct solution is *that it is stable with respect to fluctuations*. If we start with the initial concentration

$$X_i + x \quad \text{for } t = 0 \quad (9)$$

where x is small, we have to show that

$$x \rightarrow 0 \quad \text{when } t \rightarrow \infty \quad (10)$$

In equilibrium thermodynamics, or in the linear range of non-equilibrium thermodynamics such calculations are not necessary since it is sufficient to show that the relevant thermodynamic potential (free energy or entropy production) is minimum. Even far from equilibrium, we showed that a velocity potential exists.

However, in general this is not so and proof of stability based on the time variation of the perturbation x has to be given. These calculations are standard in hydrodynamics. We will see that indeed there exists situations involving sequences of auto-catalytic reactions for which the thermodynamic solution cannot be extended to far from equilibrium conditions. For sufficiently large values of the affinities characterizing the steady state, an instability appears. This instability leads to a new steady state whose major characteristic is that it is no more homogeneous in space. It leads to a discontinuous decrease of entropy. The most fascinating aspect of this instability is “symmetry breaking”.

9.2 Chemical Oscillations

Consider first oscillating chemical reactions corresponding to rotation around the stationary state (see Chpt. 8, sec. 4-5). Lotka's example of an auto-catalytic reactions;



The concentrations A and B are given and constant. All forward kinetic constants are set equal to 1 and the backwards equal to k . The reaction rates are then

$$v_1 = AX - kX^2 \quad (12)$$

$$v_2 = XY - kY^2 \quad (13)$$

$$v_3 = Y - kB \quad (14)$$

Such oscillating chemical reactions should have importance in biological clocks.

The total affinity of the reactions (11) from

$$A = \mathcal{R}T \log \frac{K(p, T)}{N_1^{\nu_1} \dots N_c^{\nu_c}} \quad (15)$$

can be shown to be

$$A = -\log k^3 R \quad (\text{in units of } \mathcal{R}T, \mathcal{R} = \text{gas constant}, K = 1) \quad (16)$$

with

$$R = B/A \quad (17)$$

The equations for the rate of change of X and Y are

$$\begin{aligned} \frac{dX}{dt} &= v_1 - v_2 = AX - XY - kX^2 + kY^2 \\ \frac{dY}{dt} &= v_2 - v_3 = XY - Y - kY^2 + kRA \end{aligned} \quad (18)$$

The steady state values X_0, Y_0 are thus

$$X_0 = 1 + kY_0 - \frac{kRA}{Y_0} \quad (\text{from (18)}) \quad (19)$$

and

$$k^3(Y_0)^4 + (1 - kA + 2k^2)(Y_0)^3 - (A - k + kRA + 2k^3RA)(Y_0)^2 + (kRA^2 - 2k^2RA)Y_0 + k^3R^2A^2 = 0 \quad (20)$$

In order to check the stability of the steady state, consider a small perturbation around the steady state:

$$X = X_0 + x(t) \quad (21)$$

$$Y = Y_0 + y(t) \quad (22)$$

Substituting these in (18) and neglecting higher order terms in x and y gives the linear homogeneous equations

$$\frac{dx}{dt} = (A - Y_0 - 2kX_0)x + (2kY_0 - X_0)y \quad (23)$$

$$\frac{dy}{dt} = Y_0x + (X_0 - 1 - 2kY_0)y \quad (24)$$

giving a solution of the form

$$x = x_0 \exp(\omega t), \quad y = y_0 \exp(\omega t) \quad (25)$$

where ω satisfies the “*dispersion equation*”

$$\omega^2 + (1 - A - X_0 + Y_0 + 2kX_0 + 2kY_0)\omega + AX_0 - 2kX_0^2 - 2kAY_0 + 4k^2X_0Y_0 - A + Y_0 + 2kX_0 = 0 \quad (26)$$

Which has two roots ω_1, ω_2 . The solution X_0, Y_0 will be stable if both roots have real parts negative.

At equilibrium the affinity vanishes and thus (16) gives

$$R = 1/k^3 \quad (\text{at equilibrium}) \quad (27)$$

giving (from (19) and (20)),

$$X_0 = A/k, \quad Y_0 = A/k^2 \quad (\text{at equilibrium}) \quad (28)$$

This solution is stable as the dispersion relation then gives two real and negative roots.

Show that the roots of (26) are real and negative at equilibrium.

However, far from equilibrium, the roots become complex.

Consider first the limiting case $k = 0$ (i.e. all reactions proceed in the forward direction only) then (19) and (20) give

$$X_0 = 1, \quad Y_0 = A \quad (\text{for } k = 0) \quad (29)$$

and (26) leads to two purely imaginary roots

$$\omega = \pm i\sqrt{A} \quad (30)$$

which describes undamped rotation around the steady state. The system cannot “forget” its initial conditions. This case $k = 0$ corresponds to *infinite affinity*,

$$|A| \rightarrow \infty \quad \text{for } k \rightarrow 0 \quad (\text{see (16)}) \quad (31)$$

whatever the values of the concentrations of the components A and B .

Let us see in detail how the steady state solutions depend on the strength of the external force (in this case on the value of $R = B/A$). For k small, ie. to first order in k , equations (19) and (20) give

$$\begin{aligned} X_0 &= 1 + kA - kR \\ Y_0 &= A - k + kA^2 \end{aligned} \tag{32}$$

Using these values in the dispersion relation (26) it can be seen that there is a critical value of $R = R_c$ such that

$$k^2(1 + A + R_c + A^2)^2 - 4A + 4k + 4kB = 0 \tag{33}$$

and such that we have complex conjugate roots (implying undamped oscillations) for all $R < R_c$, and normal aperiodic behavior for $R > R_c$.

9.3 Dissipative Structures

Hydrodynamic instabilities can be treated in a similar way to equilibrium phase transitions using the methods of non-linear thermodynamics of irreversible processes.

Consider the Bénard problem in classical hydrodynamics. A horizontal fluid layer is heated from below. The strength of the temperature gradient is measured in terms of a dimensionless quantity known as the Rayleigh number Ra , proportional to the temperature gradient.

For small values of Ra the fluid remains at rest but for a critical value of Ra there is an abrupt onset of thermal convection.

We have both dissipative and convective processes. A local potential has been determined for this situation (see Glansdorff and Prigogine, *Physica* **30**, 351 (1964)) using equation (8.15). The result is of form

$$\Phi = (\text{dissipative processes}) - (\text{convective processes}) \tag{34}$$

where each set of parentheses represents a positive contribution. This provides an interesting analogy with the free energy $F = E - TS$ in equilibrium.

For the fluid at rest the only quantity which enters in Φ is the dissipation due to thermal conduction.

For fluid in motion, we have viscous dissipation as well. Therefore, Φ starts at a positive value even for $Ra = 0$. It increases more slowly with Ra because as seen from (34) convective processes decrease the value of Φ .

This is a striking analogy of the liquid-solid transition in terms of the free energy. Here a decrease in temperature leads to a transition from a less ordered phase to a more ordered phase.

In the hydrodynamic case, an increase of the constraint (temperature gradient) leads from a situation in which the whole of the energy is in thermal motion to a much more organized state in which part of the energy is in macroscopic motion. Its entropy is less than that of a system in which the whole of the energy is in thermal motion. The loss of entropy is of the order

$$\Delta S = -E_{kin}/\bar{T} \quad (35)$$

where \bar{T} is the average temperature characterizing the system. The existence of the Bénard instability prevents the extrapolation from equilibrium to non-equilibrium conditions, just like the liquid to solid transition prevents the extrapolation from high to low temperatures.

Note that the entropy production due to dissipation increases in a discontinuous way at the Bénard transition. Since the potential Φ is equal at the transition for both the state at rest and the state with convection, (34) gives

$$(dissipative\ processes)_I - (convective\ processes)_I = (dissipative\ processes)_{II} - (convective\ processes)_{II} \quad (36)$$

Suppose that I is the state without convection, then

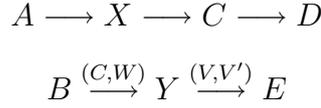
$$(dissipative\ processes)_{II} - (dissipative\ processes)_I = (convective\ processes)_{II} \geq 0 \quad (37)$$

The Bénard instability leads to an *increase* of dissipation. The thermodynamic efficacy of the system is increased. If at some moment the system could be isolated, the transport of heat by both conduction and convection would equalize the temperature more rapidly.

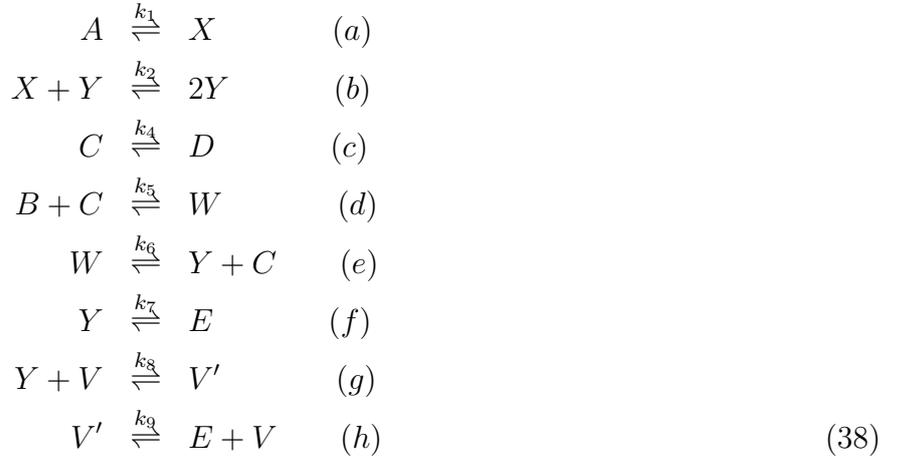
9.4 Symmetry Breaking Instabilities – The Turing Mechanism

Stability properties of the steady state in a system of autocatalytic chemical reactions.

Initial products A and B are transformed into final products D and E through intermediate products X and Y and by action of the catalysts C, W, V, V' .



Specifically, consider the following set of chemical reactions (Turing, 1952);



With the two overall reactions



Since reaction (f) in (38) is the sum of reactions (g) and (h), we must have

$$k_{-7}k_8k_9 = k_7k_{-8}k_{-9}$$

Recalling that

$$A = RT \log \frac{K(T)}{C_1^{\nu_1} \dots C_c^{\nu_c}}$$

and that $K(T) = \vec{k} / \overleftarrow{k}$. In equilibrium we have

$$\begin{aligned} X_{eq} &= \frac{k_1}{k_{-1}} A \\ Y_{eq} &= \frac{k_{-7}}{k_7} E = \frac{k_5 k_6}{k_{-5} k_{-6}} B \\ C_{eq} &= \frac{k_{-4}}{k_4} D \\ W_{eq} &= \frac{k_5 k_{-4}}{k_{-5} k_4} B D \\ V_{eq} &= \frac{k_9}{k_{-9}} V' \\ V' &= \text{arbitrary given parameter } (> 0) \end{aligned} \tag{40}$$

and

$$\begin{aligned} \left(\frac{AB}{D}\right)_{eq} &= \frac{k_{-1}k_3k_{-4}k_{-5}k_{-6}}{k_1k_2k_4k_5k_6} \\ \left(\frac{B}{E}\right)_{eq} &= \frac{k_{-5}k_{-6}k_{-7}}{k_5k_6k_7} \end{aligned} \quad (41)$$

These last two reactions are the laws of mass action for the two reactions (39).

Considering now the situation out of equilibrium, as in previous examples, the “constraints” will be the affinities of the overall reactions (39), or equivalently the dimensionless ratios

$$\frac{AB}{D} / \left(\frac{AB}{D}\right)_{eq} \quad \text{and} \quad \frac{B}{E} / \left(\frac{B}{E}\right)_{eq}$$

To determine the stationary state, we put the net flows of the unconstrained variables equal to zero. The steady state calculations are lengthy, details can be found in the original articles (see A.M. Turing, Phil. Trans. Roy. Soc. London, B237, 37 (1952), and I. Prigogine, G. Nicolis, J. Chem. Phys., 46, 3542 (1967)).

Here we only present the results. Consider the steady state solutions in two regions;

I) Near to equilibrium: Includes solutions (40) and (41) as special cases. Since it can be shown that the variation of the entropy production due to a fluctuation is always positive, this steady state solution is stable. The stability proof includes both *homogeneous* perturbations as well as *space dependent* perturbations;

$$X - X_0 = x_0 \exp(\omega t + i \frac{r}{\lambda}) \quad (42)$$

which allow for perturbations to vary from one point to another of the system. Here λ is the wavelength of the perturbation, and r is a geometrical coordinate. Whatever the wavelength λ , the characteristic frequencies are negative and the system returns to the homogeneous state.

II) Far from equilibrium: For example, when all inverse kinetic constants can be neglected

$$k_{-1} = k_{-4} = k_{-5} = \dots = k_{-9} = 0 \quad (43)$$

In this case it is found that there is a unique homogeneous steady solution. Stability of this steady state is again investigated with respect to perturbations of form (42) by including diffusion (since the perturbations can bring the system into an inhomogeneous state).

Result – for a certain range of values of the kinetic constants and the diffusion constants, the steady homogeneous solution becomes unstable. However, there now exists a new *space-dependent steady state* solution which is stable to perturbations.

This result is for infinite affinities, however, considering non-zero reverse reactions, it is possible to calculate the critical affinity above which the thermodynamic solution becomes unstable. In the in homogeneous state which is stable beyond the critical point, the production of the final substance E is especially favored in the center of the system, while the production of the other final product D is produced at a space independent rate. Correspondingly, B is consumed mainly near the center.

Further, the overall reaction rate is increased at the transition at the critical point. The system beyond the transition can therefore be characterized as a kind of “factory” in which a better subdivision of work leads to an increased “efficiency”. Similar to the Bénard instability.

9.5 General Comments

We have seen that the response of systems placed into non-equilibrium conditions can take quite different forms:

near equilibrium we have the theorem of minimum entropy production

far from equilibrium we can have reorganizations which *increase* the value of the dissipation (entropy production).

It is most probable that such instabilities (eg. Bénard's or Turing's) should play an essential role in biological processes, and in the first biogenesis steps.

Biological structures can only originate in a dissipative medium and be maintained by a continuous supply of energy. Biological structures are always linked to inhomogeneities or differentiation in space and the instability which we have studied provides a link between inhomogeneities and dissipation. Moreover, such dissipative structures exist for only narrow limits of the values of the parameters because of the required delicate balance between reaction rates and diffusion (see articles cited above). If we introduce a "poison" to alter one of these factors, the whole organization would collapse. Similar to the well know biological fact that a cell with practically the same chemical composition may be alive or dead.