MEDICAL UNIVERSITY – PLEVEN
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DIVISION OF PHYSICS AND BIOPHYSICS, HIGHER MATHEMATICS AND INFORMATION TECHNOLOGIES

LECTURE No6

NON-EQUILIBRIUM THERMODYNAMICS

Linear non-equilibrium thermodynamics. Definition and basic terms. Force and motion. Phenomenological coefficients. Conjugated fluxes.

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Non-equilibrium thermodynamics

Non-equilibrium thermodynamics - a branch of thermodynamics concerned with studying time-dependent thermodynamic systems, irreversible transformations and open systems.

It is most successful in the study of stationary states, where there are nonzero forces, flows and entropy production, but no time variation.

Physiological steady state

1. Constant flow of matter and release of waste products of metabolism

2. Constant loss of free energy, which maintains the constant concentration of substances in the system

3. Constant values of thermodynamic parameters, including internal energy and entropy

In non-equilibrium thermodynamics it is entropy (S) that takes center stage.

Irreversible transformations are characterized by a net entropy production.

Non-equilibrium thermodynamics applies to situations where the system under study is not in thermodynamic equilibrium but can be broken into subsystems which are sufficiently small to be in equilibrium, while still being large enough that thermodynamics is applicable to them.

Differences or gradients of intensive parameters are called thermodynamic forces, and they cause flows of the extensive variables.

Force and motion

A sphere is rolling downhill. It is moving spontaneously from a position with a higher potential energy to one with a lower potential energy. The direction of its movement follows a force vector (X) and is, consequently, determined by the negative gradient of the energy E_p **X = -grad** E_p.

If consideration of the energy gradient is confined to the direction of the x-coordinate, this equation can be simplified to give:

$$X_x = -\frac{dE_p}{dx} i,$$

E.g. Force acting on a charge *(q)* in an electric field in the x-direction.

Suppose there is no other gradient in the x-direction, neither ***P***, nor ***T***, nor $\boldsymbol{\mu}$ are functions of x. We can introduce the field strength (**E**) in accordance with the definition of electrical potential. The equation cannot be applied to practical calculations of ion transport because only the transport of a charge is considered.

In contrast to the movement of an electron, the transport of ions always means that there is an additional change in concentration. For transport of a noncharged substance , the negative gradient of its chemical potential is the driving force. For transport of ions, the negative gradient of electrochemical potential is the driving force.

There are many kinds of movement in biological systems that are the concern of biophysics - electron transfer, structural changes of molecules, chemical reactions, fluxes of molecules and ions, streaming of liquids in the body, and finally, mechanical movements of limbs and whole bodies.

Fluxes occupy a central position in the study of movements in biology, and therefore these will be considered here for the sake of simplicity, as a sort of generalized movement.

If a constant force acts on a body, then the latter accelerates. However, as the velocity of this body increases, the friction is likely to increase too.

When both the driving force and the frictional force become the same amount, then the body will move with a constant velocity. This is a special case of a stationary state, the so-called stationary motion.

If a comparatively minor force acts on a body, then the body will attain a velocity that is proportional to the force. This is a region where a linear analysis of irreversible thermodynamics is applicable. If the same body is more forcibly moved, then the frictional force will increase in a stronger way, and a non-linear approach is necessary.

This concept has a more general application.

A linear approach to a general equation of motion can be formulated. The flux equation can be written as follows:

$$J_i = c_i u_i X_i$$

Process	Flow	Thermodynamic force
Diffusion	Flow of non-charged particles	Concentration gradient
Electrodiffusion	Flow of charged particles (ions)	Gradient of electrochemical potential
Electrical current	Flow of electrons	Electric potential gradient
Flow of liquid	Volume flow	Hydrostatic pressure gradient

Linear nonequilibrium thermodynamics. Conjugated fluxes

If different kinds of motions and forces occur simultaneously in a system, they will influence each other. Let us consider again the flux (J_i) as a generalized kind of motion. The linear nonequilibrium thermodynamics allows us to write down a set of phenomenological equations forming a flux matrix. It includes the idea whereby all forces and fluxes in the system are coupled with each other.

$$J_n = L_{n1}X_1 + L_{n2}X_2 + L_{n3}X_3 + \ldots\ldots + L_{mn}X_n$$

The parameters L_{mn} , the phenomenological coefficients, are also called *coupling coefficients*, *cross coefficients*, or *Onsager coefficients*. (The equation was first used by L. Onsager in 1931). This general set of equations in reality is reduced, because a flux J_m is coupled with a force X_n only when $Lmn \neq 0$.

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Dissipative function. Entropy and Stability

The second principle of thermodynamics states that an isolated system moves spontaneously towards maximum entropy. When this state is achieved, then the system is in thermodynamic equilibrium.

The *entropy production* is always positive, but can approach zero asymptotically.

The condition $\sigma = 0$ means an idealized reversible process. Thermodynamically, a process is defined as being reversible if it can be repeated an arbitrary number of times without requiring the supply of additional energy.