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Non-Equilibrium Thermodynamics
M.Sc. 2nd Semester
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Topic: Introduction to Non-Equilibrium Thermodynamics

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Equilibrium thermodynamics:

Macroscopic objects have a huge number of degrees of freedom – typically of the order 10^{23}. Their characterization can be vastly simplified by choosing the relevant set of macroscopic variables that coarse grain the 10^{23} microscopic degrees of freedom. Mechanics enables us to describe the behaviour of these macroscopic variables, whereas thermodynamics treats the consequences of ignoring the vast majority of the degrees of freedom, in particular the transfer of energy to and from them. The equilibrium state is characterised by the macroscopic variables such as internal energy U, the volume V , and the mole numbers of the chemical components, Ni . Thermodynamics can be framed in two equivalent ways: the energy and the entropy representations . Although the energy representation is typically used as the basis for thermodynamic potentials, the entropy representation lends itself to the calculation of fluctuations in the system and to non-equilibrium where entropy production plays a central role.

Non-equilibrium thermodynamics or irreversible thermodynamics, the branch of science mostly founded by Ilya Prigogine (born 1917, Russia; Nobel prize in Chemistry, 1977) discusses about irreversible (non-equilibrium) processes. In any irreversible process the entropy of the universe increases: this gives the concept of entropy production here. Any irreversible process always occurs because of some generalized forces or affinities (e.g., difference in chemical potential, difference in temperature, difference in electrical potential etc.) which result in some generalized fluxes or flows (chemical reaction and diffusion, heat flow, current flow etc. respectively; such fluxes indicate the speed of the irreversible process). Non-equilibrium thermodynamics puts forward some generalized linear relations among such forces and fluxes (called phenomenological relations; those relations are generalizations from observed irreversible phenomena), and looks for the possible interrelation among the coefficients involved there. While looking for such interrelations, it notes that the irreversible phenomena at a microscopic level are governed by reversible laws, i.e., the mechanical equations of motion of individual particles are symmetric with respect to time; this concept is called that of microscopic reversibility.

For a system within which an irreversible process occurs, the infinitesimal entropy change dS because of that process can be expressed as a sum of two parts:

(i)   the entropy flow d_eS into the system from the exterior i.e., the surroundings, and

(ii)   the internal entropy production d_iS inside the system, such that $dS = d_eS + d_iS$.

As d_eS is nothing but the negative of the entropy change of the surroundings [i.e., $d_eS = - dS_{surr}$, this is because the irreversible process under consideration

is assumed to occur within the system only, thus implying that the entropy change in the surroundings (dS_{surr}) can occur solely due to a *transfer* of entropy ($-d_eS$) from the system towards it], it is obvious that d_iS (= $dS - d_eS$ = $dS + dS_{surr}$) is nothing but the entropy change of the universe (dS_{univ}). So (*i.e., as $d_iS = dS_{univ}$*) the internal entropy production is never negative (as per the 2nd law of thermodynamics *stated in terms of entropy*); it is positive for irreversible processes and zero for reversible (equilibrium) processes. For an isolated system $dS = d_iS$ as d_eS obviously equals 0.

As an example of entropy production in an irreversible process, let us consider a system consisting of two sub-systems 1 and 2, maintained respectively at two uniform temperatures T_1 and T_2 (see figure).
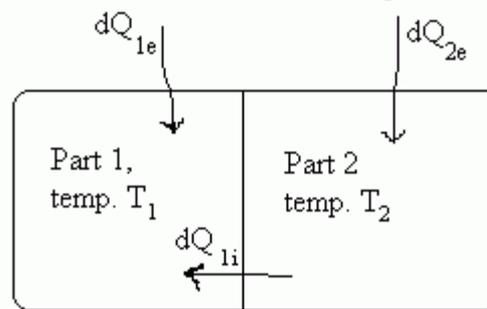
Spontaneous heat-flow between subsystems at diff. teperatures

Entropy being an extensive property, it is obvious that $dS = dS_1 + dS_2$. Let the heat absorbed by each sub-system be divided into two parts as: $dQ_1 = dQ_{1i} + dQ_{1e}$ and $dQ_2 = dQ_{2i} + dQ_{2e}$, where dQ_{1i} is the heat absorbed by sub-system 1 from sub-system 2 (i.e., from the *interior* of the system) and dQ_{1e} is the heat absorbed by sub-system 1 from the surroundings (*exterior*), and similarly for dQ_{2i} & dQ_{2e} (obviously, $dQ_{1i} = -dQ_{2i}$). Thus we get that the entropy change for the whole system dS is: $dS = dQ_1/T_1 + dQ_2/T_2 = dQ_{1e}/T_1 + dQ_{2e}/T_2 + dQ_{1i}(1/T_1 - 1/T_2)$. Remembering $dS = d_eS + d_iS$, it becomes obvious that the part $[dQ_{1e}/T_1 + dQ_{2e}/T_2]$ equals the entropy flow d_eS reversibly transferred from the surroundings to the system, so that the remaining part $[dQ_{1i}(1/T_1 - 1/T_2)]$ is the internal entropy production d_iS arising from the irreversible heat flow inside the system; i.e., $d_iS = dQ_{1i}(1/T_1 - 1/T_2)$.

It is obvious that the internal entropy production is always positive here: from our familiar zeroth law of thermodynamics, we find that $dQ_{1i} > 0$ if $T_1 < T_2$, $dQ_{1i} < 0$ if $T_1 > T_2$ and $dQ_{1i} = 0$ if $T_1 = T_2$. Thus dQ_{1i} and $(1/T_1 - 1/T_2)$ will *have the same sign* or, at most, both will be zero, excluding the possibility for any negative value for the internal entropy production. It can be zero when thermal equilibrium is established, i.e. when $T_1 = T_2$. The quantity d_iS/dt,

entropy production per unit time, is frequently used in irreversible thermodynamics, and is called the rate of entropy production. Here, $d_iS/dt = (dQ_{1i}/dt)(1/T_1 - 1/T_2)$. It is obvious that this rate is never negative as d_iS is also never negative. This equation also signifies an important concept: the rate of entropy production is a product of the rate dQ_{1i}/dt of the irreversible process of heat flow (a generalized flow or flux), and of a generalized driving force or affinity $\{(1/T_1 - 1/T_2)$, the difference of inverse of temperatures$\}$ which is a function of state of the system. The direction of the irreversible process is determined by the sign of this function, and this driving force may be considered the *macroscopic cause* of the irreversible process.

Aims of non-equilibrium thermodynamics

The purpose of non-equilibrium thermodynamics is to answer questions about systems out of equilibrium. Here we consider linear irreversible thermodynamics that is based on the balance equations (conservation of mass, momentum etc.) and the linear relation between forces and fluxes from symmetry and phenomenological considerations, following. non-equilibrium thermodynamics provides a prescription for determining the dynamics of a system that is out of equilibrium, with a few assumptions. Essentially the recipe is as follows:

1. Choose the relevant slow variables of the system, typically conserved quantities and broken symmetry variables.
2. Write down the balance equations for the conserved variables.
3. Write down the (redundant) entropy balance equation and identify the entropy production (sources of dissipation).
4. Identify the force (F) - current (j) pairs in the entropy production.
5. Write down the phenomenological constitutive equations, ensuring they obey the relevant symmetries e.g. Onsager relations.
6. Use the constitutive equations to substitute for the unknown fluxes in the equations of motion.

In looking for the steady state of the system there are some analogies with equilibrium thermodynamics. In equilibrium thermodynamics the maximum entropy principle can be used to find equilibrium (this is a postulate in some formulations of thermodynamics). In non-equilibrium thermodynamics the steady state can be characterized, in some systems, by a minimum in the dissipation, or entropy production of the system.

Identifying hydrodynamic variables

1. Due to the assumption of local equilibrium the variables of equilibrium thermodynamics U, S, V, N, ... and T, p, μ, ... vary slowly (both spatially and in time).
2. Conserved variables, e.g. mass, particle number, etc. are slow because it takes a finite time to transport them.
3. Systems with broken symmetries have extra variables, such as the lattice distortion in crystals or the nematic director in liquid crystals, which exhibit slow dynamics (Goldstone's theorem → broken symmetry variables are slow in the limit of large wavelength).

Equations of motion

The equation of motion for the system is typically one of force balance between reversible (reactive) and irreversible (dissipative) forces.

$$F_{rev} + F_{irrev} = 0$$

Dissipation occurs because of the coarse-grained nature of the description of the system. We transfer energy from the macroscopic variables with which we describe the system, into some of the microscopic variables that were thrown away in the coarse graining process. Time reversal symmetry, which is the basis of the Onsager relations, can be used to classify the terms in the equations of motion and identify them as either reversible or irreversible and gain insight into the equation of motion.

Reference:

1. http://www.angelfire.com/pro/riturajkalita/irrevtherm.htm
2. M. L. Bellac, F. Mortessagne, and G. G. Batrouni, Equilibrium and Nonequilibrium Statistical Thermodynamics. Cambridge, 2004.
3. S. R. de Groot and P. Mazur, Non-equilibrium thermodynamics. Dover Publications, 1984.
4. P. D. Olmsted, "Lectures on irreversible thermodynamics." 2001.