ENTROPY – HISTORICAL ANALYSIS

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Abstract: The way of entropy concept in the case of the phenomenological and statistical analysis methods is completed. The analysis of entropy in the study of variational processes, discrete structures, fluctuation and dynamical systems is presented.

Keywords: entropy, variation processes, discrete structures.

BASIC CONCEPTS

In 1865, German physicist Clausius introduced the concept of entropy depending only on the initial and final states of a reversible process. If S_1 and S_2 are entropy values in the states 1 and 2,

$$S_1 - S_2 = \int_1^2 \frac{dQ}{T} \quad \text{or} \quad ds = \frac{dQ}{T} \tag{1}$$

In an irreversible cycle the smaller proportion of the initial value of entropy Q_1 transforms to work. Then the expression of the entropy function for the reversible and irreversible processes is as follows:

$$\text{for the reversible } dS = \frac{dQ}{T} = 0, \quad \oint dS = \oint \frac{dQ}{T} = 0,$$

$$\text{for an irreversible cycle } dS > \frac{dQ}{T}, \quad \oint dS = 0, \quad \oint \frac{dQ}{T} < 0 \tag{2}$$

In general for the system it can be written

$$\oint \frac{dQ}{T} \le 0. \tag{3}$$

For the "external environment" which the system exchanges heat with as dQ has of opposite sign, we have

$$\oint \frac{dQ}{T} \ge 0. \tag{4}$$

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At the end of the cycle, both reversible and irreversible, there is no change in entropy as the system is returned to its initial state. For irreversible cycles, this means that the system transfers more heat to the environment, typically by converting mechanical energy into heat in the irreversible processes. Consequently, the entropy of the environment increases.

That the change in entropy can be written as the sum of two terms:

$$dS = d_eS + d_iS. \tag{5}$$

Here d_eS – the change in the entropy of the system due to the exchange of energy and matter, and d_iS – the change in entropy due to irreversible processes within the system. For a closed system that does not exchange matter with the environment $d_eS = dQ / T$. The value d_eS can be positive or negative, and d_iS – only greater than or equal to zero.

The evolution of an arbitrary state to a state of equilibrium is the result of irreversible processes. At equilibrium, these processes terminate. Thus, the non-equilibrium state can be defined as one in which irreversible processes are forcing the system to evolve to a state of equilibrium.

LOCAL ENTROPY PRODUCTION

The second law of thermodynamics must be a local law. Divide the system into r pieces. Then

$$d_iS = d_iS^1 + d_iS^2 + \dots + d_iS^r \geq 0 \tag{6}$$

where d_eS^k – the entropy production of the k-th, and for each k

$$d_iS^k \geq 0. \tag{7}$$

Undoubtedly, the statement that the entropy production in every part of the system caused by the irreversible processes, – positive value, is more stringent than the classical formulation of the second law (entropy of an isolated system can only increase or remain unchanged). Note that the second law of thermodynamics, formulated in such a manner does not require the system to be isolated. This is true for all systems independently of the boundary conditions.

Local increase in entropy in continuous media may be determined using the entropy density $s(x, t)$. As in case of total entropy $ds = d_is + d_es$, and $d_is \geq 0$. We define the local entropy production as follows:

$$\sigma(x,t) \equiv \frac{d_is}{dt} \geq 0. \tag{8}$$

$$\frac{d_is}{dt} = \int_V \sigma(x,t)dV. \tag{9}$$

For irreversible processes that can be studied experimentally, non-equilibrium thermodynamics is based on an explicit expression for σ. Before presenting this expression, we write the explicit equations of local power balance and local concentrations.

MINIMUM ENTROPY PRODUCTION

In a thermodynamic system, the various forces F_k ($k = 1, 2, ..., n$) correspond to different streams I_k. The system can be located far from equilibrium, keeping some forces F_k ($k = 1, 2, ..., s$) for fixed nonzero values and leaving the rest of the forces F_k ($k = s + 1, ..., n$) free. In this case, streams suitable withheld forces reach constant values (I_k = const, where $k = 1, 2, ..., s$), while the free forces reduce the respective streams to zero $I_k = 0$ ($k = s + 1, ..., n$).

In the linear mode, the total entropy production of the systems for the flow of energy and matter $ds / dt = \int \sigma dV$ (where σ – the generation of entropy) in the equilibrium state reaches a minimum value. This provision, the so-called "principle of least dissipation of entropy", was proposed by Rayleigh.

GIBBS FREE ENERGY AND CHEMICAL POTENTIAL

A great contribution to the thermodynamics of chemical processes belongs to Josiah Willard Gibbs. He considered the heterogeneous system consisting of a number of homogeneous parts, each of which contained substances $S_1, S_2, …, S_n$ with masses $m_1, m_2, …, m_n$.

Assuming that the change in energy dU of a homogeneous part should be proportional to the mass of matter $dm_1, dm_2, …, dm_n$, Gibbs suggested the following equation, which is valid in any homogeneous part of the system:

$$dU = TdS - pdV + \mu_1 dm_1 + \mu_2 dm_2 + …+ \mu_n dm_n, \tag{10}$$

where μ_k – the chemical potential.

It is inconvenient to describe chemical reactions using the change of the mass of the reactants. It is much more familiar and easier to use for this change in the number of moles, since the rates of chemical reactions and diffusion laws easier to formulate using molar quantities. We write the equation (10) expressing the amount of substance in moles:

$$dU = TdS - pdV + \mu_1 dN_1 + \mu_2 dN_2 + …+ \mu_n dN_n. \tag{11}$$

Taking into account the dependence (11) we have

$$d_i S = -\frac{1}{T} \sum_1^n \mu_k d_i N_k > 0 \tag{12}$$

For a closed system $d_e N_k = 0$. The rate of chemical reaction by the component k is determined dN_k / dt, so the entropy production can be written as follows:

$$d_i S = -\frac{1}{T} \sum_1^n \mu_k \frac{dN_k}{dt} > 0 \qquad (13)$$

To distinguish between external forces and the external environment, we express material changes in moles dN_k as

$$dN_k = d_i N_k + d_e N_k, \qquad (14)$$

where $d_i N_k$ – changes due to irreversible processes, $d_e N_k$ – changes due to exchange of substances with the environment.

Relation (14) allows to record the change in entropy for this process as follows:

$$d_i S = \frac{dU + pdV}{T} - \left(\frac{\mu_2 - \mu_1}{T}\right) d\xi = \frac{dU + pdV}{T} + \frac{A}{T} d\xi \qquad (15\text{–}16)$$

If $dU + pdV = 0$ then the transfer of particles leads to a change in entropy, given by the formula

$$d_i S = -\left(\frac{\mu_2 - \mu_1}{T}\right) d\xi > 0 \qquad (17)$$

The second law of thermodynamics requires that the value is positive, i.e. transfer of particles takes place from a field of high chemical potential to low chemical potential. This is the process of diffusion: the particles of high concentration transfer to low concentration.

Above we were talking about homogeneous systems. Thermodynamic dependences can be formulated with the help of entropy $sT(x)$, $m_k(x)$, which is a function of the temperature and density of number of moles.

We express the energy and entropy density as a function of the local temperature $T(x)$ and the density of number of moles $n_k(x)$ (both values are available for direct measurement)

$$\begin{aligned} u &= u[T(x), n_k(x)], \\ s &= s[T(x), n_k(x)]. \end{aligned} \qquad (18)$$

The total entropy and the total energy of the system are obtained by integrating, respectively, the entropy density and energy density in terms of the system:

$$\begin{aligned} S &= \int_V s[T(x), n_k(x)] dV, \\ U &= \int_V u[T(x), n_k(x)] dV. \end{aligned} \qquad (19)$$

Since the whole system is not in thermodynamic equilibrium, the total entropy S is generally not a function of total energy U and the total volume V. However, the thermodynamic description remains possible if the temperature is well defined at each point in space.

Isochoric-isothermal potential $F = F(V, T, N, x_i)$ of the Helmholtz free energy. Between the Gibbs free energy and Helmholtz free energy there is a relationship

$$
\begin{aligned}
F &= U - TS, \\
H &= V + pG, \\
G &= F + pV.
\end{aligned}
\tag{20}
$$

With the help of these dependences it can be defined the conditions of thermodynamic equilibrium and stability.

FUNDAMENTALS OF NON-EQUILIBRIUM THERMODYNAMICS

The evolution of an arbitrary state to a state of equilibrium is the result of irreversible processes. The temperature in all parts of the system in this state becomes the same.

However, the even temperature distribution is not one of the requirements under which the entropy and energy of the system is well-defined. For non-equilibrium systems, in which the temperature is not evenly distributed, but locally it is defined, we can introduce the density of such thermodynamic quantities (potentials) as energy and entropy. For example, the energy density

$$
U[T(x), n_k(x)] = \text{internal energy per unit volume}
\tag{21}
$$

can be determined by the local temperature T and a molar density $n_k(x)$ equal number of moles per unit volume.

Similarly, the density of entropy $s(T, nk)$ can be determined. Then, the total energy U, the total entropy S and the total number of moles N can be expressed by the corresponding density:

$$
S = \int_V s[T(x), n_k(x)]dV,
\tag{22}
$$

$$
U = \int_V u[T(x), n_k(x)]dV,
\tag{23}
$$

$$
N = n_k(x)dV.
\tag{24}
$$

In general, each of these variables – the total energy U, the entropy S, the number of moles N and the volume V – is not a function of the other three variables. Generally irreversible change d_iS is connected with flow of a quantity dX, e.g. heat

or substance during time dt. For $dX = dQ$, where dQ – the amount of heat that is transferred during dt; for $dX = dN$, where dN – number of moles of substance that have moved (transformed) for the time dt. In both cases, the change in entropy can be written as

$$d_i S = F dX, \qquad (25)$$

where F – the thermodynamic force. In this formalism thermodynamic forces have to be recorded as functions of thermodynamic variables, such as temperature and concentration. For the flow of matter corresponding to the thermodynamic force can be expressed by analogy. All irreversible processes can be described in terms of thermodynamic forces and thermodynamic flows. Entropy changes are the sum of all the changes caused by the irreversible flows dX_k, that allows us to generalize:

$$d_i S = \sum_k F_k dX_k \geq 0 \quad \text{or} \quad \frac{d_i S}{dt} = \sum_k F_k \frac{dX_k}{dt} \geq 0. \qquad (26)$$

Inequality (26) expresses the second law of thermodynamics. Entropy production by every irreversible process is the product of the corresponding thermodynamic force F_k and flow $J_k = dX_k / dt$.

THE ENTROPY BALANCE EQUATION

The derivation of the entropy balance should be based on the equation of conservation of energy balance by the number of moles. The last equation contains expressions for the entropy flow I_S and entropy production σ, which is caused by irreversible processes, such as thermal conductivity, diffusion and chemical reaction. Entropy balance equation has the form

$$\frac{ds}{dt} + \nabla \cdot J_s = \sigma \qquad (27)$$

To obtain the explicit form of J_S and σ it is necessary to proceed as follows. To simplify this we consider the system in the absence of external fields and dissipation of kinetic energy due to convection or diffusion. Using Gibbs relation $Tds = du - \sum \mu_k dn_k$ we can write:

$$\frac{ds}{dt} = -\frac{1}{T}\frac{du}{dt} - \sum_k \frac{\mu_k}{T} \cdot \frac{dn_k}{dt}. \qquad (28)$$

Now considering the balance equation for the number of moles and the internal energy balance equation where $d(KE) / dt = 0$, the expression can be written as

$$\frac{\partial s}{\partial t} = -\frac{1}{T}\nabla \cdot J_u + \sum_k \frac{\mu_k}{T}\nabla \cdot J_k - \sum_{k,j}\frac{\mu_k}{T}\nu_{jk}\upsilon_j. \tag{29}$$

This equation can be simplified and written in the form (27), taking into account the following observations. Firstly, the affinity A_j of reaction j has the form

$$A_j = -\sum_k \mu_k \nu_{jk}. \tag{30}$$

Second, if g – scalar function and J – vector, then

$$\nabla \cdot (gJ) = J \cdot (\Delta g) + g(J \cdot \Delta). \tag{31}$$

In view of (30) and (31), and after some straightforward transformations you can rewrite entropy balance (29) as follows:

$$\frac{ds}{dt} + \nabla \cdot \left(\frac{J_u}{T} - \sum_k \frac{\mu_k J_k}{T}\right) = J_u \cdot \nabla \frac{1}{T} - \sum_k J_k \cdot \nabla \frac{\mu_k}{T} + \sum_j \frac{A_j \nu_j}{T}. \tag{32}$$

Comparing this equation with (26), we obtain that

$$J_s = \left(\frac{J_u}{T} - \sum_k \frac{\mu_k J_k}{T}\right) \tag{33}$$

$$\sigma = J_u \cdot \nabla \frac{1}{T} - \sum_k J_k \cdot \nabla \frac{\mu_k}{T} + \sum_j \frac{Aj\upsilon j}{T} \geq 0. \tag{34}$$

This expression – one of the options for the second law recording: $\sigma > 0$.

GENERAL INFORMATION ABOUT THE STATISTICAL THERMODYNAMICS OF HAMILTON, THE THEORY OF ENSEMBLES

In classical mechanics, the state of a point particles system is usually described by the coordinates $q_1, \ldots, q_s$, and moments $p_1, \ldots, p_s$. A particularly important role is played by the energy of the system, written in these variables.

Usually it has the form

$$H = E_i(p_1, \ldots, p_s) + V_i(q_1, \ldots, q_s), \tag{35}$$

where the first term depends on pulses and is kinetic energy, and the second depends only on coordinate and corresponds to the potential energy. Equation (35) is a Hamiltonian function. The basic idea of ensemble concept introducing is that instead of a dynamical system, as it is customary in the Hamiltonian system, you consider the set of systems according to the same Hamiltonian. Gibbs ensemble

can be represented as a set of points in phase space. The evolution of the system state as a function of time is usually determined by the Hamiltonian $H = p(q, p)$. Note that the Hamiltonian function is used in the classical calculus of variations to represent the Euler equation of mechanical systems motion in canonical form.

The values p and q satisfy the equation of motion:

$$\dot{q} = \frac{\partial H}{\partial p}, \quad \dot{p} = \frac{\partial H}{\partial q}. \tag{36}$$

We introduce generalized current vector in phase space $\dot{J} = (\dot{q}, \dot{p})$.

From equation (36), that

$$div\dot{I} = \frac{\partial \dot{q}}{\partial q} + \frac{\partial \dot{p}}{\partial p} \equiv 0, \tag{37}$$

i.e., phase fluid is not compressed.

Differential form of the law of number of particles conservation is the equation of continuity in phase space:

$$\frac{\partial f}{\partial t} + div(Jf) = 0,$$

or (according to the conditions)

$$\frac{\partial f}{\partial t} + \dot{q}\frac{\partial f}{\partial q} + \dot{p}\frac{\partial f}{\partial p} = 0. \tag{38}$$

Equation (38) is called the Liouville equation. Its current components $J = (q, p)$ are expressed as a function p, q (and possibly, t). The following notice is significant: the equation (38) does not contain any information other than that which follows from the equation of motion (36). It follows from the properties of partial differential equations of the first order. The solution (39) can be written as:

$$f(q, p, t) = q_0(q, p, t), \quad p_0 = p_0(q, p, t) \tag{39}$$

where the relationship between (q_0, p_0) and (q, p) is defined by (35), and $f_0 = f_0(q_0, p_0) = f(t = 0)$ – the initial condition.

Let $f(q, p, t)$,

$$\frac{dS[f]}{dt} = 0, \tag{40}$$

where

$$S[f] = -\int f \ln f dp dq. \tag{41}$$

Expression (40) is determined from (41) by differentiating

$$\frac{dS[f]}{dt} = \int (1 - \ln f) \frac{df}{dt} dpdq. \tag{42}$$

Since, according to the Liouville equation $\frac{df}{dt} = 0$. It follows that the entropy defined by the distribution function f does not change with time.

THE BOLTZMANN EQUATION

Analyzing the relationship between the microscopic behavior of the environment and the macroscopic laws of thermodynamics, Boltzmann introduced his famous relation between entropy and probability.

$$S = k \ln W, \tag{43}$$

where W – static mass of the state, described by a distribution function f; k – Boltzmann constant. Detailed discussion and the formula (42) deduction were given by Ehrenfest. Further development of the various branches of science (statistical physics, information theory, etc.) confirms that depth knowledge of nature, which is inherent in the Boltzmann equation.

Information interpretation of entropy can define distributions of statistical physics: the Gibbs canonical distributions, i.e. distribution corresponding to the maximum value of information.

Einstein, using the Boltzmann idea in other way, proposed a formula for estimating the probability of fluctuations of thermodynamic quantities:

$$P(\Delta s) = Ze^{k/\Delta s}, \tag{44}$$

where Δs – the change in entropy associated with the fluctuation relative to state of equilibrium, Z – the normalized constant providing the sum of all probabilities equal to one.

ENTROPY THEORY OF DYNAMICAL SYSTEMS

One of the major directions of the entropy analysis method refers to the theory of probability information developed by Kolmogorov, who, using the basic tenets of the theory of information, introduced the concept of entropy theory of dynamical systems, also known as K-entropy, which is denoted by h. The formal definition of a typical for any physical situation K-system consists of the following: this is Hamiltonian system, wherein

$$h > 0. \tag{45}$$

In general case $h \neq 0$.

Kolmogorov's work on entropy has begun a rigorous analysis of dynamical systems in the limiting case.

Here are the main properties of the K-entropy.

1. Entropy h determines the rate of entropy change S as a result of the purely dynamic process of trajectories moving in phase space.

2. The entropy h, the growth rate of local instability h_0 and inverse time of tripping time correlations h_c are of the same order:

$$h \sim h_0 \sim h_c. \tag{46}$$

Thus the physical meaning of K-entropy reveals.

3. Entropy h is a metric invariant of the system, i.e. its value is not dependent on the method of phase space partitioning and coarsening.

4. Systems with the same value of entropy h, in some sense isomorphic to each other, that is, the statistical laws of motion of such systems should be the same.

The concept of entropy can be applied to the thermodynamic non-equilibrium states, if the deviation from equilibrium thermodynamics are small and it can be introduced the concept of local thermodynamic equilibrium in the small but still macroscopic scale. In general, the entropy of a nonequilibrium system is the sum of the entropies of its parts which are in local equilibrium.

The thermodynamics of nonequilibrium processes allows more detailed study of the process of increasing entropy and calculate the amount of entropy generated per unit volume of time due to deviations from thermodynamic equilibrium.

Statistical physics associates the entropy with the probability of the macroscopic state of the system. Entropy is defined by the logarithm of the statistical weight Ω of reduced equilibrium state:

$$S = k \ln \Omega(E, N), \tag{47}$$

where $\Omega(E, N)$ – number of quantum-mechanical equations in a narrow energy range ΔE near the value of energy E of the system of N particles, in classical statistical physics Ω – the value of volumes in the phase space of the system for given E and N.

First connection between the entropy and the probability of the system was established by Boltzmann. The evolution of a closed system is in the direction of the most probable distribution of energy for individual subsystems. Statistical physics considers a particular class of processes – the fluctuations for which the system becomes less likely position, and its entropy decreases. The presence of fluctuations shows that the law of entropy increase is only performed on average for a large period of time.

The entropy in statistical physics is closely related to the information entropy, which is a measure of uncertainty messages (messages are described by many

variables x_1, x_2, ..., x_n and probabilities P_1, P_2, ..., P_n of these values occurrence in the message). For a certain (discrete) statistical probability distribution P_k information entropy is called the value

$$S_k = -\sum_{k=1}^{n} P_k \ln P_k \quad \text{when} \quad \sum_{k=1}^{n} P_k = 1. \tag{48}$$

$S_k = 0$, if the number of P_k is equal to one, and the rest – to zero, i.e., the information is credible, there is no uncertainty. Entropy has the largest value when all P_k are the same (maximum uncertainty in the information). Information entropy, as a thermodynamic one, has the property of additivity. With the probabilistic interpretation of information entropy can be deduced basis of distribution of statistical physics: the canonical Gibbs distribution corresponding to the maximum value of information entropy.

CONCLUSION

Entropy is a measure of the energy loss (irreversible) of phenomena taking place in many areas of production: heat and mass transfer, physicochemical, dispersed structures, fluctuations etc. In the future, with the advent of new technical solutions entropy, no doubt, will be playing the role of valuation measure of excellence in the energy field of the investigated phenomena.

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