

Entropy equilibrium equation and dynamic entropy production in environment liquid*

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Abstract The entropy equilibrium equation is the basis of the nonequilibrium state thermodynamics. But the internal energy implies the kinetic energy of the fluid micelle relative to mass center in the classical entropy equilibrium equation at present. This internal energy is not the mean kinetic energy of molecular movement in thermodynamics. Here a modified entropy equilibrium equation is deduced, based on the concept that the internal energy is just the mean kinetic energy of the molecular movement. A dynamic entropy production is introduced into the entropy equilibrium equation to describe the dynamic process distinctly. This modified entropy equilibrium equation can describe not only the entropy variation of the irreversible processes but also the reversible processes in a thermodynamic system. It is more reasonable and suitable for wider applications.

Keywords: nonequilibrium thermodynamics, entropy equilibrium equation, entropy production, irreversible processes, environment liquid.

Development of thermodynamics in recent years can not only replace the inequality of the second law in classical thermodynamics with an equality, but also explain the mechanism of the forming and maintaining of macroscopic ordering structure in general, so that the irreversible processes can be described quantitatively^[1~3]. This is achieved through generalizing the concept and method of the equilibrium state thermodynamics to the nonequilibrium state and irreversible processes in terms of the local equilibrium hypothesis. A series of important conclusions about the linear and nonlinear nonequilibrium state thermodynamics have been drawn using the entropy equilibrium equation. It means that any change in the thermodynamic property of a system will change the conclusions of the linear or nonlinear nonequilibrium state thermodynamics. Obviously, the entropy equilibrium equation is the important basis of the nonequilibrium state thermodynamics.

The entropy equilibrium equation is derived from Gibbs relation under the condition of local equilibrium hypothesis. The internal energy in Gibbs relation is the total kinetic energy of molecular heat movement in the classical thermodynamics. However, the internal energy in the entropy equilibrium equation is the total energy minus the total system potential energy and the kinetic energy of the mass center^[3,4]. It

means that the system internal energy in the entropy equilibrium equation comprises the macroscopic kinetic energy of the fluid micelle movement relative to mass center, which is not strictly the internal energy in the classical thermodynamics, namely the mean kinetic energy of the molecular movement. So the system entropy variation caused by the kinetic energy of macroscopic movement of the fluid micelle is not reflected in the entropy equilibrium equation. It is not a serious problem for fluid under the condition of laboratory scale, but it will be a serious problem for environmental hydrodynamics under the condition of the earth scale about atmosphere and ocean. The fluid micelle is situated in earth force field (gravity and Coriolis force). The kinetic energy of macroscopic movement of the fluid micelle in the earth force field is extremely important for the system entropy variation. This fact restricts the applicability of the current nonequilibrium state thermodynamics to the environmental hydrodynamics^[5]. Thus, the current entropy equilibrium equation must be modified.

1 Reviewing the deduction of classical entropy equilibrium equation

It is necessary to review the deduction of the classical entropy equilibrium equation for analytical convenience. Under the condition of local equilibrium hypothesis, the Gibbs relation can be written as

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$$\frac{d\bar{s}}{dt} = \frac{1}{T} \frac{du}{dt} + \frac{p}{T} \frac{dv}{dt} - \frac{1}{T} \sum_{n=1}^l \tilde{\mu}_n \frac{dc_n}{dt}, \quad (1)$$

where the entropy in unit mass is \bar{s} ; the chemical potential in unit mass is $\tilde{\mu}_n$. The mass of 1 mole of the n th constituent in a system is M_n , so the relation between the chemical potential in 1 mole and the chemical potential in unit mass is

$$\mu_n = M_n \tilde{\mu}_n. \quad (2)$$

The continuity equation is

$$\frac{dv}{dt} = \frac{1}{\rho} \frac{\partial U_j}{\partial x_j}, \quad (3)$$

the equilibrium equation of the n th constituent in the system can be written as

$$\rho \frac{dc_n}{dt} = - \frac{\partial J_{nj}^m}{\partial x_j} + \sum_{r=1}^m \nu_{nr} M_n \omega_r, \quad (4)$$

and the internal energy equation is

$$\rho \frac{du}{dt} = - \frac{\partial J_{qi}}{\partial x_j} - p \frac{\partial U_j}{\partial x_j} - \Pi_{ij} \frac{\partial U_i}{\partial x_j} + \sum_{n=1}^l J_{nj}^m F_{nj}. \quad (5)$$

The symbols T , u , v , and c_n in the above equations are the fluid temperature, internal energy, specific volume and ratio of the n th constituent in the system respectively; p , U_j , Π_{ij} , F_{nj} , J_{nj}^m , J_{qi} the hydrostatic pressure, velocity component in j direction, stress tensor, external force in j direction enduring the n th constituent in the system, material flux in j direction partaking in the m th chemical reaction of the n th constituent in the system and heat flux in j direction respectively; ω_r , ν_{nr} the reaction rate and stoichiometric coefficient partaking in the r th chemical reaction of the n th constituent in the system respectively; t the time, and x_j the space coordinate.

Put Eqs. (3~5) into Eq. (1) to get the entropy variation equation

$$\rho \frac{d\bar{s}}{dt} = - \frac{1}{T} \frac{\partial J_{qi}}{\partial x_j} + \sum_{n=1}^l \frac{\mu_n}{T} \frac{\partial J_{nj}^m}{\partial x_j} - \frac{1}{T} \Pi_{ij} \frac{\partial U_i}{\partial x_j} + \frac{1}{T} \sum_{n=1}^l J_{nj}^m F_{nj} - \sum_{n,r=1}^{l,m} \frac{\nu_{nr} \mu_n}{T} \omega_r, \quad (6)$$

after arranging suitably, we get the entropy equilibrium equation in unit volume

$$\frac{\partial s}{\partial t} = - \frac{\partial J_{sj}}{\partial x_j} + \sigma. \quad (7)$$

This is the classical entropy equilibrium equation in the nonequilibrium state thermodynamics, in which s is the entropy in unit volume. By entropy additivity principle, the relationship between entropy in unit volume and entropy in unit mass should be

$$ds = \rho d\bar{s}. \quad (8)$$

The entropy flow and entropy production are respec-

tively given by

$$J_{sj} = sU_j + \frac{1}{T} J_{qj} - \sum_{n=1}^l \frac{\mu_n}{T} J_{nj}, \quad (9)$$

$$\sigma = J_{qj} \frac{\partial}{\partial x_j} \left(\frac{1}{T} \right) + \sum_{n=1}^l J_{nj} \left[- \frac{\partial}{\partial x_j} \left(\frac{\mu_n}{T} \right) + \frac{F_{nj}}{T} \right] - \frac{1}{T} \Pi_{ij} \frac{\partial U_i}{\partial x_j} + \sum_{r=1}^m \frac{\mathcal{A}_r}{T} \omega_r, \quad (10)$$

where J_{sj} is the entropy exchange rate in j direction through unit area, called for short as the entropy flow; σ represents the rate of producing entropy, called for short as the entropy production. A chemical affinity \mathcal{A}_r is defined by

$$\tilde{\mathcal{A}}_r = - \sum_{n=1}^l \nu_{nr} \tilde{\mu}_n, \quad \mathcal{A}_r = M_n \tilde{\mathcal{A}}_r. \quad (11)$$

Eqs. (7, 9 and 10) constitute the classical equilibrium equation in the nonequilibrium state thermodynamics.

2 Modifying the entropy equilibrium equation in force field

Subtracting the potential energy of all constituents $\psi = \sum_n c_n \psi_n$ and the kinetic energy of mass

center $\frac{1}{2} U_j^2$ from the total energy ϵ , we get the internal energy u in equilibrium equation (5)^[3,4], which means that the internal energy u still contains the macroscopic kinetic energy of the constituents' movement relative to mass center. The internal energy should only comprise the thermal vibration and the short-range interaction among molecules in thermodynamic sense. Hence, we should subtract the potential energy and kinetic energy of all constituents from the total energy ϵ then focusing on the internal energy u^* in unit mass

$$u^* = \epsilon - \sum_{n=1}^l c_n \psi_n - \sum_{n=1}^l \frac{1}{2} c_n U_{nj}^2. \quad (12)$$

On the other hand, the total kinetic energy should be sum of kinetic energy $\frac{1}{2} U_j^2$ of the mass center and

the kinetic energy $\frac{1}{2} c_n (U_{nj} - U_j)^2$ of all the constituents' movement relative to mass center, namely

$$\sum_{n=1}^l \frac{1}{2} c_n U_{nj}^2 = \frac{1}{2} U_j^2 + \sum_{n=1}^l \frac{1}{2} c_n (U_{nj} - U_j)^2, \quad (13)$$

where U_{nj} is the velocity component in j direction of the n th constituent. The total energy density and the potential energy of all constituents are

$$\epsilon = \frac{1}{2} U_j^2 + \psi + u, \quad \psi = \sum_{n=1}^l c_n \psi_n,$$

where ψ_n is the potential energy in unit mass of the n th constituent in the system. Considering the above formulas, the internal energy of molecular heat movement u^* is exactly equal to the internal energy u , as defined in the current classical nonequilibrium state thermodynamics, minus the kinetic energy of constituents relative to mass center, namely

$$u^* = u - \sum_{n=1}^l \frac{1}{2} c_n (\mathbf{U}_{nj} - \mathbf{U}_j)^2. \quad (14)$$

Gibbs relation of the equilibrium state is really the relationship among the entropy \bar{s} , the internal energy u^* of thermal vibration and molecular short-range interaction, and c_n , i. e.

$$T d\bar{s} = du^* + p dv - \sum_{n=1}^l \bar{\mu}_n^* dc_n. \quad (15)$$

Introducing the chemical potential $\bar{\mu}_n^*$, the relationship between which and u^* is

$$\sum_{n=1}^l c_n \bar{\mu}_n^* = u^* - T\bar{s} + pv. \quad (16)$$

Since the hypothesis of local equilibrium is yet tenable, Eq. (15) is tenable in the deviating equilibrium state, then Eq. (1) is changed into the form

$$\frac{d\bar{s}}{dt} = \frac{1}{T} \frac{du^*}{dt} + \frac{p}{T} \frac{dv}{dt} - \frac{1}{T} \sum_{n=1}^l \bar{\mu}_n^* \frac{dc_n}{dt}. \quad (17)$$

Putting Eq. (14) into Eq. (17), and using the relation of matter diffusion flow of the n th constituent

$$\mathbf{J}_{nj}^m = \rho c_n (\mathbf{U}_{nj} - \mathbf{U}_j),$$

we get

$$\begin{aligned} \frac{d\bar{s}}{dt} &= \frac{1}{T} \frac{du}{dt} + \frac{p}{T} \frac{dv}{dt} - \frac{1}{T} \sum_{n=1}^l \bar{\mu}_n \frac{dc_n}{dt} \\ &\quad - \frac{1}{\rho T} \sum_{n=1}^l \mathbf{J}_{nj}^m \frac{d}{dt} (\mathbf{U}_{nj} - \mathbf{U}_j), \end{aligned} \quad (18)$$

where the relation of $\bar{\mu}_n$ with $\bar{\mu}_n^*$ obeys

$$\bar{\mu}_n = \bar{\mu}_n^* + \frac{1}{2} (\mathbf{U}_{nj} - \mathbf{U}_j)^2 \quad (19)$$

and the relation between u and $\bar{\mu}_n$ is similar to Eq. (16)

$$\sum_{n=1}^l c_n \bar{\mu}_n = u - T\bar{s} + pv. \quad (20)$$

When $\frac{d(\mathbf{U}_{nj} - \mathbf{U}_j)}{dt}$ equals zero, namely the derivative of velocity of each constituent's movement relative to mass center with respect to time can be neglected, Eq. (18) is the same as Eq. (1). Also, if the acceleration of mass center is neglected, Eq. (1) is true.

In the same way as the derivation of Eq. (6), using Eqs. (3~5), the modified entropy equilibrium equation in the force field can be obtained from

Eq. (18)

$$\begin{aligned} \frac{\partial \bar{s}}{\partial t} &= - \frac{\partial}{\partial x_j} \left(s \mathbf{U}_j + \frac{1}{T} \mathbf{J}_{qj} - \sum_n \frac{\mu_n}{T} \mathbf{J}_{nj} + \frac{\mathbf{U}_i}{T} \Pi_{ij} \right) \\ &\quad + \mathbf{J}_{qj} \frac{\partial}{\partial x_j} \left(\frac{1}{T} \right) - \sum_n \mathbf{J}_{nj} \left[\frac{\partial}{\partial x_j} \left(\frac{\mu_n}{T} \right) \right. \\ &\quad \left. + \frac{1}{T} \left(\frac{d}{dt} (\mathbf{U}_{nj} - \mathbf{U}_j) - \mathbf{F}_{nj} \right) \right] \\ &\quad + \Pi_{ij} \frac{\partial}{\partial x_j} \left(\frac{\mathbf{U}_i}{T} \right) - \sum_{n,r} \frac{\nu_{nr} \mu_n}{T} \omega_r. \end{aligned} \quad (21)$$

This equation shows that the entropy equilibrium equation should include the acceleration of the constituents relative to mass center. Using the relation of matter diffusion flow of the n th constituent, separating the terms relating with the acceleration of constituent relative to mass center and the external force from the entropy production, the entropy equilibrium equation (21) can be written as

$$\frac{\partial \bar{s}}{\partial t} = - \frac{\partial}{\partial x_j} \mathbf{J}_{sj} + \sigma + \sigma_f, \quad (22)$$

$$\mathbf{J}_{sj} = s \mathbf{U}_j + \frac{1}{T} \mathbf{J}_{qj} - \sum_n \frac{\mu_n}{T} \mathbf{J}_{nj} + \Pi_{ij} \frac{\mathbf{U}_i}{T}, \quad (23)$$

$$\begin{aligned} \sigma &= \mathbf{J}_{qj} \frac{\partial}{\partial x_j} \left(\frac{1}{T} \right) - \sum_n \mathbf{J}_{nj} \frac{\partial}{\partial x_j} \left(\frac{\mu_n}{T} \right) \\ &\quad + \Pi_{ij} \frac{\partial}{\partial x_j} \left(\frac{\mathbf{U}_i}{T} \right) - \sum_{n,r} \frac{\nu_{nr} \mu_n}{T} \omega_r, \end{aligned} \quad (24)$$

$$\begin{aligned} \sigma_f &= \rho \frac{1}{T} \frac{d}{dt} \sum_n c_n \left[\frac{1}{2} (\mathbf{U}_{nj} - \mathbf{U}_j)^2 \right] \\ &\quad + \rho \sum_n \mathbf{U}_{nj} \frac{c_n \mathbf{F}_{nj}}{T} + \rho \mathbf{U}_j \frac{\mathbf{F}_j}{T}. \end{aligned} \quad (25)$$

This is named the revised form of the entropy equilibrium equation. A new term, called the "dynamic entropy production" σ_f , is added to the revised entropy equilibrium equation, which characterizes the contribution of reversible processes to entropy exchange. The entropy flux [Eq. (23)] and the entropy production [Eq. (24)] are entirely similar to Eqs. (9 and 10), except that the momentum transportation of molecular viscosity, the molecular thermal conduction and the molecular diffusion are all included in the molecular viscosity transportation.

3 Physical significance of entropy equilibrium equation and concept of dynamic entropy production

The various terms in the entropy equilibrium Eq. (22) as well as those in the entropy flow Eq. (23) and the entropy production Eq. (24) all have explicit physical significance:

- (i) The entropy equilibrium equation (22)

shows that the local variation of the entropy is the algebraic sum of the following three terms, i. e. the divergence of the entropy flow, the entropy production and the dynamic entropy production. Eq. (22) is the mathematical expression of the second law of thermodynamics under the condition of the local equilibrium hypothesis. (ii) The first term on the right side of Eq. (23) represents entropy flow due to convection processes; the second term is due to thermal conduction; the third and fourth terms are the entropy flow due to matter diffusive processes and viscous flow. (iii) The first term on the right side of Eq. (24) is related with thermal conduction; the second term is related with diffusive processes; the third term is related with viscous flow; and the fourth term is related with chemical reactions. The various terms in this formula are all composed of two factors related with the rate and impetus of irreversible processes. For example, the thermal conduction flow \mathbf{J}_q , the matter diffusive flow \mathbf{J}_n and the momentum flow or stress tensor $\frac{\mathbf{\Pi}_{ij}}{T}$, as well as the chemical reaction rate ω_r , are all the rates of irreversible processes. These rate factors can be generally called the thermodynamic flow of irreversible processes. The other factors of these terms in the formula are related with the impetus leading to corresponding "flow". For example, the temperature gradient $\frac{\partial}{\partial x_j} \left(\frac{1}{T} \right)$ leads to the heat flow; the chemical potential gradient $-\frac{\partial}{\partial x_j} \left(\frac{\mu_n}{T} \right)$ leads to the diffusive flow; the velocity gradient $-\frac{\partial U_i}{\partial x_j}$ leads to the momentum flow, while $\frac{\mathcal{A}_r}{T}$ can be regarded as the impetus of the chemical reaction. These factors related with impetus can be generally called the thermodynamic force of the irreversible processes. The entropy production can be characterized as the strength of the irreversible processes, because the entropy production is the product of the rate of irreversible processes and the impetus force of irreversible processes.

A new term σ_f is added to the entropy equilibrium Eq. (22), which consists of three terms: the first term is the kinetic energy variation of the fluid micelle relative to mass center, the second term is the work done on the constituents by external force, and the third term is the work done by external force on

the micelle mass center. They have the dimension of entropy production, if they are divided by temperature. Therefore σ_f is called the "dynamic entropy production". Because the work done by external force on the micelle and its mass center may be positive or negative, the dynamic entropy production does not have the definite positive property. In the physical essence, the kinetic energy variation and all the works done by external forces obey the dynamic reversible process of the second law. It means that the dynamic entropy production is not the strength measure of the irreversible process, but is the strength of the dynamic reversible process. Though the dynamic entropy production has the same dimension as the entropy production, its physical essence is similar to entropy flow. The entropy flow in Eq. (23) is the entropy transported by airflow and the entropy variation due to internal energy transportation with molecular viscosity, thereby leading to system entropy variation.

Just owing to the qualitative difference between the classical entropy equilibrium Eq. (7) and the revised entropy equilibrium Eq. (22), their capabilities in describing the properties of a thermodynamic system are distinctly different. The revised entropy equilibrium equation is even more reasonable in physics. For example, the author ever studied the property of equilibrium state of an atmospheric system using the classical entropy equilibrium equation, yet fell into the predicament of "equilibrium state paradox of the atmospheric system", but he attained reasonable conclusions using the revised entropy equilibrium equation^[5]. Again for instance, the least entropy production principle is an important theorem proved by Prigogine^[3] in the linear region of nonequilibrium state thermodynamics. But it is difficult to prove this theorem in the nonlinear region using the classical entropy equilibrium equation. However, the author¹⁾ has proved this theorem in the nonlinear region of nonequilibrium state thermodynamics in an atmospheric system using this revised entropy equilibrium equation. Again, Glansdorff and Prigogine^[6] inducted the excessive entropy as a Lyapunov function to study the stability of thermodynamic system. But the excessive entropy inducted by them contains only the

1) Hu, Y. Q. Least principle of entropy production and order structure of nonlinear thermodynamic system, (to be published)

irreversible processes of molecular viscosity transport. By all means, the stability of any thermodynamic system is not only related with the irreversible processes of molecular viscosity transport, but also must be related with the dynamic reversible processes of external forces. To overcome this difficulty, they inducted the general kinetic energy with velocity disturbance superimposed on the excessive entropy as a Lyapunov function. These facts sufficiently demonstrate that it is of theoretical significance and practical importance to induct the dynamic entropy production into the entropy equilibrium equation.

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