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A thermodynamical study of the clockwork hypothesis proposed by E. Schrödinger

Etsuro Ito[a,*], Eiji Shiomitsu[b], Hideo Suzuki[b]

[a]*Division of Biological Sciences, Graduate School of Science, Hokkaido University, North 10, West 8, Kita-ku, Sapporo 060-0810, Japan*

[b]*Department of Physics, School of Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan*

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Abstract

In the present study, the 'clockwork' hypothesis proposed by Schrödinger was examined from the viewpoint of thermodynamics. Firstly, noticing a unidirectional transfer of entropy in a heat engine, the logic was briefly explained about a close relation between this entropy transfer and an irreversible cycle performed by a working body. Next, paying attention to two fundamental differences between a heat engine and a biological system, we considered an isolated system A_Σ consisting of three one-component systems (A_i, A, A_o) and noted a case that the same molecules as the component ones flowed quasistatically into A_i from the outside. Then, the unidirectional flows of the molecules, energy and entropy, which were induced by the above inflow in A_Σ, were formulated on the basis of the equilibrium thermodynamics for an open system. Furthermore, it was clarified that the fundamental equation for these flows is the Schrödinger inequality and that the necessary-sufficient condition for this inequality is the existence of an irreversible cycle performed by A. Here A corresponds to a working body in a heat engine. It was, thus, concluded that the 'clockwork' hypothesis by Schrödinger is considered to be reasonable for a biological system composed of various irreversible subsystems. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Clockwork; Negative entropy; Irreversible cycle; Schrödinger inequality; Clausius inequality

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[*] Corresponding author. Tel.: +81-11-7062615; fax: +81-11-7064448.
E-mail address: eito@sci.hokudai.ac.jp (E. Ito).

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1. Introduction

In 1944, Erwin Schrödinger published '*What is Life? — The Physical Aspect of the Living Cell*', in which he advocated the need and significance of the following three strategies about the construction of molecular biology [1]: (1) to investigate the substance of genes and to explain the mechanism of heredity on the basis of the genes; (2) to grasp the orderliness of various irreversible systems, which are constituent elements of biological systems, from such a viewpoint that 'a living organism feeds upon negative entropy'; and (3) to examine the validity of 'clockwork' in biological systems, because the orderliness of whole biological systems is considered to be supported by the mechanism of 'clockwork'.

The scientists influenced strongly by the above proposal (1) won the Nobel prizes. For example, Wilkins, Crick, Watson, and Monod, Jacob, Lwoff, and also Delbrück, Luria, Hershey won the Prizes in Physiology and Medicine in 1965, 1969 and 1962, respectively [2]. About the proposal (2), Brillouin made up his original information theory in which he esteemed the concept of 'negative entropy' and placed an emphasis upon a close relation between 'negative entropy' and amount of information [3]. As was pointed out by us previously [4], however, the real motive of Schrödinger, who described 'a living organism feeds upon negative entropy', was to emphasize the following point paradoxically: because the metabolism system of substances and energy in cells is equipped with an ingenious entropy-transmission system, the entropy ΔS_o released to the outside of the system is larger than the entropy ΔS_i absorbed into the inside:

$$\Delta S_i - \Delta S_o < 0. \tag{1}$$

It is well known that a working body in a heat engine in such a 'negative entropy condition' undergoes an irreversible cycle and performs work to the outside.

The 'clockwork' hypothesis of the above proposal (3) was based on a concept that 'the most striking features of living matter are visibly based to a large extent on the 'order-from-order' principle' (see [1] p. 80). To understand its rationality, if we suppose that the irreversible subsystems composing a biological system are all in the 'negative entropy condition', it would be natural to consider that an 'order-from-order' mechanism is certainly furnished in this biological system. Moreover, if the irreversible subsystems undergo the 'irreversible cycles' as like a working body in a heat engine does, these irreversible cycles would correspond to the 'gears' in 'physical clockwork', and hence this 'order-from-order mechanism' could certainly establish the 'clockwork'. The 'clockwork' hypothesis of proposal (3) is thus, conceivable as the rational conclusion that can be derived directly from the concept of 'negative entropy' in the proposal (2).

The purposes of the present study are to prove that: (a) the inequality (1), which we call the Schrödinger inequality, is considered to be the fundamental equation for unidirectional transfers of substances, energy and entropy in a biological system; and (b) its necessary-sufficient condition is the existence of an irreversible cyclic system, based on the equilibrium thermodynamics for an open system and also on a necessarily minimum model. The validity of the 'clockwork' hypothesis by Schrödinger as mentioned above is thus grasped theoretically.

For these purposes, the present paper is composed of five sections. First, to construct the necessarily minimum model by clearing up the similarities and differences between a heat engine and a biological system, we confirm in Section 2 that no work to the outside can be obtained just by contacting two objects, and thus we clarify the reason why a working body must exist between a high- and a low-temperature heat source in a heat engine. Next, for the same purpose as Section 2, we confirm in Section 3 that the Clausius inequality, which has entirely the same form and content as the Schrödinger inequality, is the fundamental equation for unidirectional transfers of entropy and energy in a heat engine, and that its necessary-sufficient condition is an irreversible cyclic change in its states performed by a working body. We thus make clear that the most important role of the working body is to absorb entropy ΔS_i (with heat Q_i) from the high-temperature (T_i)

heat source to start the engine and then to release entropy ΔS_o (with heat Q_o; $\Delta S_o > \Delta S_i$) to the low-temperature (T_o) heat source to return finally to its initial state, and that owing to this entropy flow, the remaining heat ($T_i \Delta S_i - T_0 \Delta S_0$) [i.e. ($Q_i - Q_o$)] can smoothly be changed into work W to a thermally-isolated external body.

The role of a working body in a heat engine as described above suggests strongly that 'Schrödinger's gear', which feeds on the 'negative entropy' is a kind of an 'irreversible cyclic system'. Therefore, in Section 4, attention is first directed to the differences between the 'irreversible subsystems' (being the constituent elements of a biological system) and a working body in a heat engine about the following two points: (A) there is not only the exchanging of energy and entropy but also the incoming and outgoing of chemical substances in the 'irreversible subsystems'; (B) a biological system does not have anything corresponding to a high- or low-temperature heat source in a heat engine, but keeps temperature and pressure almost constant by using various irreversible subsystems composing the biological system.

Next, based on the above-mentioned consideration of the similarities and differences between a heat engine and a biological system, we consider an isolated system A_Σ consisting of three one-component systems (A_i, A, A_o) and note a case that ΔN_Σ mol of the same molecules as the component ones did flow quasistatically into A_i from the outside. Needless to say, the inflow of the molecules of ΔN_Σ mol, which initially changes the internal energy of A_i, is indispensable to A_Σ as an energy source of the work to its outside for the reason (B) described above, and this inflow must be considered as a quasistatic process because we intend to treat A_Σ on the basis of the 'equilibrium' thermodynamics for an open system. Then, the unidirectional flows of molecules, energy and entropy, which are induced by the above inflow in A_Σ, are formulated according to the equilibrium thermodynamics, and it is clarified that the fundamental equation for these flows is the Schrödinger inequality and that the necessary-sufficient condition for this fundamental equation is the existence of an irreversible cycle performed by A.

Finally, in Section 5, we notice that the 'irreversible cyclic systems' satisfying the inequality (1) correspond to the 'gears' that feed on the negative entropy, as proposed by Schrödinger, and hence that the systems composed of such 'irreversible cyclic systems' possess the structure of 'clockwork'. Based on these results, we conclude the validity of 'clockwork' hypothesis proposed by Schrödinger for biological systems. In addition, we point out that when a working body A performs an irreversible cyclic change in its states, the maximum amount of work done by A is closely related to a change in 'exergy', but not to a change in Gibbs free energy.

2. No work to the outside can be obtained only by direct contact between two objects

In a heat engine, a working body performing an irreversible cycle, which is a 'gear' in a wide sense, must be located between a high- and a low-temperature heat source because of the following two reasons: (1) no work to the outside can be obtained only by direct contact between two different heat sources; and (2) an irreversible cycle performed by a working body is the necessary-sufficient condition for unidirectional transfers of entropy and energy in a heat engine. The purpose of this section is to grasp the first reason quantitatively. This is because the explanation to this fundamental issue is hardly given in the usual textbooks regarding thermodynamics. For example, the following brief explanation was given in the famous textbook by Landau and Lifshitz [5]: Let us find the maximum amount of work which can be done in the exchange of a small quantity of energy between two bodies at different temperatures; First of all we must emphasize that if the transfer of energy were to be brought about by direct contact between the two bodies, then no work at all would be done; Hence, to bring about a reversible transfer of energy and thus to obtain the maximum work, it is necessary to introduce some auxiliary body ('working body') which performs a certain reversible cyclic process (see [5] p. 56).

Therefore, to understand the content of the implication of the above sentences, we consider in this section a change (ΔS) in the entropy during the period of heat transfer in the system, in which a high-temperature (T_i) heat source A_i is brought into contact with a low-temperature (T_o) heat source A_o to transfer heat quantity Q from A_i to A_o. For simplicity, we assume that these two sources compose a thermally isolated system as a whole, and that their volume and heat capacity (C_i and C_o) at a constant volume are constant independently of the transfer of Q.

When both the sources reach the thermal equilibrium at temperature T_e after the transfer of heat quantity Q, we have

$$T_e = (C_o T_o + C_i T_i)/(C_o + C_i),$$
$$Q = C_o C_i (T_i - T_o)/(C_o + C_i), \tag{2a}$$

$$\Delta S = C_o \log(T_e/T_o) + C_i \log(T_e/T_i). \tag{2b}$$

Next, to confirm whether or not this ΔS is positive, let us assume for simplicity that

$$\Delta T_s \equiv T_i - T_o, \quad (\Delta T_s/T_o)^2 \ll 1. \tag{3a}$$

Then Eq. (2b) can approximately be expressed as

$$\Delta S \approx [C_o C_i/(C_o + C_i)](\Delta T_s/T_o)^2/2 > 0. \tag{3b}$$

This result shows that the system consisting of A_i and A_o is a thermally isolated system as was assumed above, and that the transfer of heat quantity Q only increases the entropy of this isolated system.

Finally, let us suppose that the internal energy and entropy of the isolated system are E and S, respectively, and that E is expressed as a function of S: $E(S)$. Since this system is isolated thermally, the positive or negative work ΔW done by changing the internal energy from $E(S)$ to $E(S + \Delta S)$ must satisfy the relation

$$E(S) = E(S + \Delta S) + \Delta W. \tag{4a}$$

Here this ΔW should be done quasistatically. Accordingly, when Eq. (3a) holds, the above equation can approximately be rewritten as

$$\Delta W \approx -(\partial E/\partial S)_V \Delta S \approx -T\Delta S < 0, \tag{4b}$$

where V is the volume of the isolated system and $T_o < T < T_i$. Therefore, no positive work to the outside can be obtained only by the direct contact between two objects.

3. Why does a working body need to perform a cyclic change in its states?

In this section, to understand the role of thermodynamics of a working body in a heat engine, which is concerned with the second reason at the beginning of Section 2, let us suppose the following situation. While a working body A changes irreversibly from a certain state to the other one with increasing its entropy by σ, a high-temperature (T_i) heat source A_i gives heat quantity Q_i to the working body A, and a low-temperature (T_o) heat source A_o gains heat quantity Q_o from the working body A, and thus a thermally isolated external body receives work W from this working body A (see Fig. 1). In this case, the whole system consisting of A_i, A and A_o can be regarded as a thermally isolated system, and hence its entropy change $\Delta\Sigma$ satisfies the relation

$$\Delta\Sigma = \sigma - Q_i/T_i + Q_o/T_o > 0 \tag{5a}$$

in accordance with the principle of increase of entropy. Here, $-Q_i/T_i$ represents the entropy decrease $-\Delta S_i$ in the high-temperature heat source A_i, and Q_o/T_o represents the entropy increase ΔS_o in the low-temperature heat source A_o [note that the entropy change in the external body which receives the work W is completely ruled out, because it is thermally isolated from (A_i, A, A_o)].

After all, when the working body performs an irreversible change in its states, the following inequality generally holds:

$$Q_i/T_i - Q_o/T_o = \Delta S_i - \Delta S_o < \sigma. \tag{5b}$$

Accordingly, the best-ordered operation man-

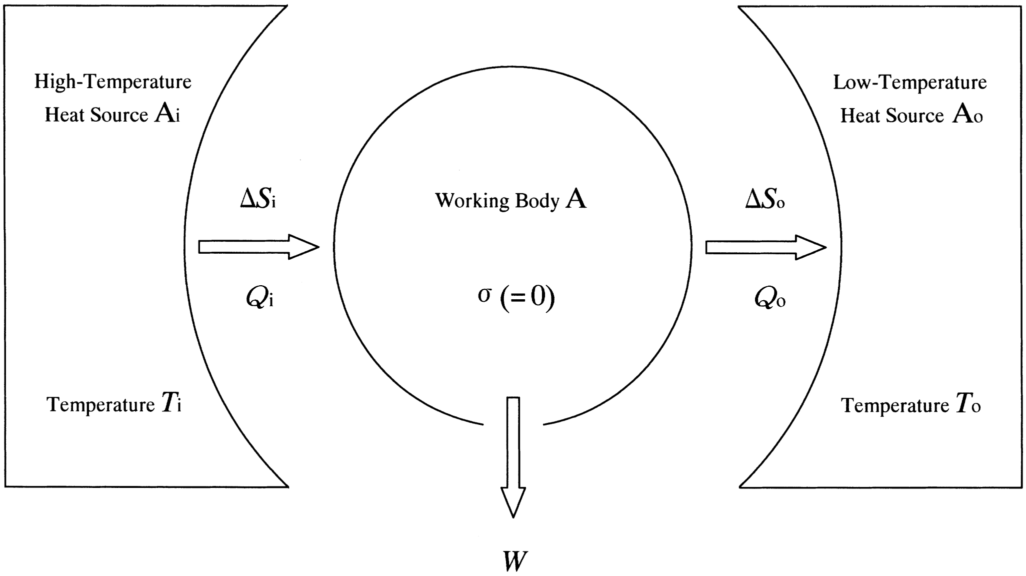

Fig. 1. Schematic representation of the inflow and outflow of energy and entropy in a working body of a heat engine.

ner is materialized in the case of $\sigma = 0$. In this case, the working body must perform an irreversible cyclic change in its states, because the entropy is a state function, which is dependent only on the thermodynamic state of the system but not on how to trace the paths to this state. Therefore, the Clausius inequality holds in this case:

$$Q_i/T_i - Q_o/T_o = \Delta S_i - \Delta S_o < 0. \tag{6a}$$

Here it should be noted that this inequality has the same form as the Schrödinger inequality (1).

Next, let us confirm that the working body satisfying the inequality (6a) can do a positive work to the external body as follows. Because Eq. (6a) can be rewritten as

$$1 - T_o/T_i > 1 - Q_o/Q_i, \tag{6b}$$

this working body can certainly do a positive work ($W = Q_i - Q_o > 0$) to the external body, provided that $T_i > T_o$ and $Q_i > Q_o$. Its efficiency ($\eta \equiv W/Q_i$) obviously satisfies the inequality

$$1 > \eta_r > \eta > 0, \quad \eta_r \equiv 1 - T_o/T_i, \tag{6c}$$

where η_r represents the efficiency of a reversible heat engine.

To sum up, the most rational change in the state of a working body in a heat engine is as follows. The working body A absorbs the entropy ΔS_i from the high-temperature heat source A_i to start the engine, and then releases the entropy ΔS_o being larger than ΔS_i to return finally to its initial state. Owing to this entropy transfer, the remaining heat quantity $(T_i \Delta S_i - T_o \Delta S_o)$ [i.e. $(Q_i - Q_o)$] is smoothly changed into the work W to the external body. Furthermore, by comparing Eq. (6a) and Eq. (5b), the existence of this irreversible cycle is found to be a sufficient condition for Eq. (6a). This is because the veracity of Eq. (6a) is generally guaranteed by the condition $\sigma = 0$.

4. The fundamental equation and its necessary-sufficient condition for unidirectional flows of chemical substances, energy and entropy

In the previous section, we paid attention to the unidirectional flows of entropy and energy in a heat engine, and clarified that the fundamental equation is the Clausius inequality [Eq. (6a)],

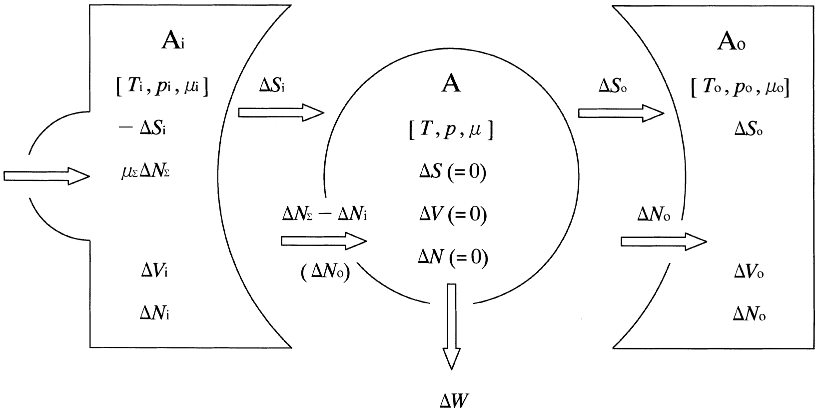

Fig. 2. Unidirectional flows of molecules, energy and entropy induced by the quasistatic inflow of the same molecules (ΔN_Σ mol) from the external medium. Numbers and symbols in small parentheses are used for the case where a one-component system A performs an irreversible cycle.

which has the same form and content as the Schrödinger inequality [Eq. (1)], and found that its necessary-sufficient condition is the existence of an irreversible cycle performed by a working body. Now, expanding the concept of ‘gears’ composing a ‘physical clockwork’, let us regard as a kind of ‘gear’ such an apparatus that transfers some physical quantities, chemical substances and so on in a certain direction. A working body in a heat engine is a typical example for this ‘gear’ in a wide sense. The various irreversible systems inducing the unidirectional flows of chemical substances, energy and entropy in a biological system are also the ‘gears’ in this wide sense. Therefore, a biological system aggregating these gears can be considered to possess a kind of ‘clockwork’. Furthermore, it would be natural for us to expect that the fundamental equation for these unidirectional flows must be the Schrödinger inequality (Eq. (1)).

However, as mentioned in Section 1, the ‘gear’ in a biological system is largely different from that in a heat engine because: (A) there are the incoming and outgoing of not only the energy and entropy but also the chemical substances in the ‘gears’ of a biological system; and (B) a biological system does not have the equipment corresponding to a high- and a low-temperature heat source that a heat engine has, but keeps its temperature and pressure almost constant by various irreversible systems composing the biological system. Thus, in this section, we assume that three one-component systems (A_i, A, A_o) compose an isolated system A_Σ and that the same molecules (ΔN_Σ mol) as their component ones flow quasistatically into A_Σ from the outside. At that time, we pay attention to the unidirectional flows of molecules, energy and entropy induced by the above flow, and consider the fundamental equation for these unidirectional flows and its necessary-sufficient condition on the basis of the equilibrium thermodynamics for an open system (see Fig. 2).

The isolated system consisting of three one-component systems (A_i, A, A_o) needs to be assumed, since no positive work to the outside can be obtained only by direct contact between two one-component systems (A_i, A_o). When A_i and A_o construct an isolated system as a whole, the state changes in accordance with the ‘principle of increase of entropy’, and hence they cannot do a positive work to the outside as was concluded from Eq. (4b), no matter what change occurs in its states [note that this issue is obvious also from our later conclusion of Eq. (9), because two conditions $\Delta S_o - \Delta S_i > 0$ and $\Delta W < 0$ can be obtained from Eq. (9) when $\Delta V_\Sigma = \Delta N_\Sigma = 0$].

Now, we define that the temperature, pressure and chemical potential (i.e. intensive variables) of three one-component systems (A_i, A, A_o) consisting of the same molecules are (T_i, p_i, μ_i), (T,

p, μ) and (T_o, p_o, μ_o), respectively, and that while the entropy, volume and mol number (i.e. extensive variables) of A change a little by ΔS, ΔV and ΔN, respectively, due to an irreversible change in the states of A, the extensive variables of (A_i, A_o) change by ($-\Delta S_i$, ΔV_i, ΔN_i) and (ΔS_o, ΔV_o, ΔN_o), respectively. Also we assume that the changes in intensive variables, (T_i, p_i, μ_i) and (T_o, p_o, μ_o), due to the above changes in the extensive variables, can completely be neglected, because the changes in these intensive variables cannot exert a significant influence on the internal energies of (A_i, A_o), as will be described below.

Furthermore, we express that the energy delivered from the outside by the molecules of ΔN_Σ mol is $\mu_\Sigma \Delta N_\Sigma$, and that the work done by A to a thermally isolated external body is ΔW. Then, based on the energy conservation law, a change ΔE in the internal energy of A can be obtained as follows:

$$\begin{aligned}\Delta E = \mu_\Sigma \Delta N_\Sigma - \Delta W + T_i \Delta S_i - T_o \Delta S_o + p_i \Delta V_i \\ + p_o \Delta V_o - \mu_i \Delta N_i - \mu_o \Delta N_o,\end{aligned} \tag{7a}$$

where $(-T_i \Delta S_i - p_i \Delta V_i + \mu_i \Delta N_i)$ and $(T_o \Delta S_o - p_o \Delta V_o + \mu_o \Delta N_o)$ represent the changes ΔE_i and ΔE_o in the internal energy of A_i and A_o, respectively.

Now, noting that there is only a very small deviation in each of the intensive variables between A_i and A_o (this is a characteristic of a biological system), we express that

$$\begin{aligned}T_i = \overline{T} + \Delta T_i, \quad p_i = \overline{p} + \Delta p_i, \quad \mu_i = \overline{\mu} + \Delta \mu_i, \\ T_o = \overline{T} - \Delta T_o, \quad p_o = \overline{p} - \Delta p_o, \quad \mu_o = \overline{\mu} - \Delta \mu_o.\end{aligned} \tag{7b}$$

Here, for example, $\overline{T}$ is nearly equal to the mean value of T_i and T_o, and we assume that the second-order terms of small amounts such as $\Delta T_i \Delta S_i$, $\Delta T_o \Delta S_o$, $\Delta p_i \Delta V_i$, $\Delta p_o \Delta V_o$, $\Delta \mu_i \Delta N_i$, $\Delta \mu_i \Delta N_o$ can all be neglected. To do so, Eq. (7a) is simplified to be

$$\begin{aligned}\Delta E \approx -\Delta W + (\mu_\Sigma - \overline{\mu}) \Delta N_\Sigma - \overline{T}(\Delta \Sigma - \Delta S) \\ + \overline{p}(\Delta V_\Sigma - \Delta V) + \overline{\mu} \Delta N; \\ \Delta \Sigma = -\Delta S_i + \Delta S + \Delta S_o, \\ \Delta V_\Sigma = \Delta V_i + \Delta V + \Delta V_o, \\ \Delta N_\Sigma = \Delta N_i + \Delta N + \Delta N_o\end{aligned} \tag{7c}$$

[note that the changes (ΔS, ΔV, ΔN) can approximately be expressed as respective linear functions of ($T - \overline{T}$, $p - \overline{p}$, $\mu - \overline{\mu}$) when A is the open one-component system of an ideal liquid, and hence that each of these changes can be considered to be correlated with the others].

On the other hand, the following equation must hold according to the principle of increase of entropy when the states of isolated system A_Σ change irreversibly:

$$\Delta \Sigma > 0, \quad \text{i.e. } \Delta S_i - \Delta S_o < \Delta S, \tag{8a}$$

where $\Delta \Sigma$ is the entropy change in A_Σ. Accordingly, by combining this equation with Eq. (7c), we obtain

$$\begin{aligned}\Delta W < -\Delta\left(E - \overline{T}S + \overline{p}V - \overline{\mu}N\right) + \overline{p}\Delta V_\Sigma \\ + (\mu_\Sigma - \overline{\mu}) \Delta V_\Sigma.\end{aligned} \tag{8b}$$

The validity of this equation can be confirmed as follows. When $\Delta N = \Delta V_\Sigma = \Delta N_\Sigma = 0$, the maximum amount of work performed by A to the external body is found to be $-\Delta(E + \overline{p}V - \overline{T}S)$ in agreement with the conclusion by Landau and Lifshitz (see [5] p. 58).

Finally, considering the case where A performs an irreversible cyclic change in its states (in other words, A behaves an irreversible cycle), we rewrite Eqs. (8a) and (8b) to obtain

$$\begin{aligned}\Delta S_i - \Delta S_o < 0, \quad \Delta W < (\mu_\Sigma - \overline{\mu}) \Delta N_\Sigma + \overline{p} \Delta V_\Sigma; \\ \Delta N_\Sigma = \Delta N_i + \Delta N_o, \quad \Delta V_\Sigma = \Delta V_i + \Delta V_o.\end{aligned} \tag{9}$$

Needless to say, the changes in the state functions of A are zero when A performs a cycle and returns to its initial state, because the extensive variables (S, V, N) and the internal energy E are the state functions.

The first equation in Eq. (9) is the Schrödinger inequality (Eq. (1)) itself, and is regarded as the general expansion of the Clausius inequality (Eq. (6a)). This first equation clearly proves that the unidirectional transfer of entropy satisfying $\Delta S_i < \Delta S_o$ is certainly induced by an irreversible cycle performed by A. Moreover, when the molecules are carried from the outside, the conditions

$$\mu_\Sigma - \bar{\mu} > 0, \quad \Delta V_\Sigma > 0 \tag{10}$$

must be satisfied, and hence the second equation in Eq. (9) indicates that A can do a positive work ΔW to the external body due to the above entropy transfer [note that the quasistatic inflow of the molecules of ΔN_Σ mol into A_i plays the most important role in Eq. (9) as the energy source of the work ΔW]. That is, there are also unidirectional flows of molecules and energy. Furthermore, by comparing the first equation in Eq. (9) and Eq. (8a), it can be found that the sufficient condition for this Schrödinger inequality is the existence of an irreversible cycle performed by A. The condition $\Delta S = 0$ guarantees sufficiently the veracity of the Schrödinger inequality.

5. Concluding remarks

The main points obtained in the present study are summarized as follows: (a) the Schrödinger inequality can be considered to be the fundamental equation for the unidirectional transfers of chemical substances, energy and entropy in a biological system; and (b) the necessary-sufficient condition for this fundamental equation is the existence of irreversible cycles performed by various irreversible subsystems composing a biological system. Accordingly, if numerous ‘irreversible cycles’ satisfying Eq. (1) are organically linked and result in constructing a system, such a system certainly possesses the structure of ‘clockwork’ as proposed by Schrödinger. As mentioned in Section 1, these ‘irreversible cycles’ are clearly in a so-called ‘negative entropy condition’, and their role corresponds to that of the ‘gears’ feeding on the negative entropy. Therefore, the two conclusions described above show not only the validity for the proposals (2) and (3) by Schrödinger but also the close relation between them both.

Next, to understand the meaning of the first term on the right-hand side of Eq. (8b), let us consider an open one-component system A and its surrounding environment body $\bar{A}$ consisting of the same component, with the definition that the internal energy, volume, entropy and mol number in A are E, V, S and N, respectively; the pressure, temperature and chemical potential in $\bar{A}$ are $\bar{p}$, $\bar{T}$ and $\bar{\mu}$, respectively. Here $\bar{p}$, $\bar{T}$ and $\bar{\mu}$ are regarded to be constant by assuming the volume of $\bar{A}$ to be very large. The minimum amount of work $\Delta R_{\min}$ performed by an external working body A_w to A is given to be $\Delta(E + \bar{p}V - \bar{T}S - \bar{\mu}N)$, where A_w is assumed to be thermally isolated from A and $\bar{A}$ ([5]; see Sec. 20). Thereby, the maximum amount of work $\Delta R_{\max}$ done by A to A_w is given by

$$\Delta R_{\max} = -\Delta R_{\min} = -\Delta\left(E + \bar{p}V - \bar{T}S - \bar{\mu}N\right), \tag{11}$$

and the absolute value of $\Delta R_{\max}$ is equal to the change ΔU in the energy defined by

$$U = E - E_0 + \bar{p}(V - \bar{V}) - \bar{T}(S - \bar{S}) - \bar{\mu}(N - \bar{N}), \tag{12}$$

where $E_0 = E(\bar{p}, \bar{T}, \bar{\mu})$; $\bar{V}$, $\bar{S}$ and $\bar{N}$ represent the volume, entropy and mol number of $\bar{A}$, respectively.

Finally, it should be noticed that U of Eq. (12) is the ‘exergy’ named by Rant [6,7], and that there are the following fundamental differences between Eq. (12) and Gibbs free energy, although they resemble each other. Because a substance system that can be considered within the equilibrium thermodynamics must be in harmony with the environment body, the value of each state variable such as temperature or pressure of the former is the same as the latter one. In contrast, when ‘exergy’ of Eq. (12) has a finite value, the substance system A possesses a different volume V, entropy S and mol number N from those in the environment body $\bar{A}$. Namely, this exergy is such an energy that takes account of the differences in extensive variables between A and $\bar{A}$.

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