Motoyosi Sugita 
and 
the Fourth Law of Thermodynamics 

Kazumoto Iguchi 

KazumotoIguchi Research Laboratory(KIRL) 

70-2 Shinhari, Hari, Anan, Tokushima 774-0003, Japan 

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Abstract 

The purpose of this lecture is to introduce to you Dr. Motoyosi Sugita, a ”widely unknown” Japanese thermodynamicist nowadays and his study on the thermodynamics of transient phenomena such as (i) the Sugita’s thermodynamics known as the fourth law of thermodynamics and (ii) his theory of life.
1. Introduction

Who knows Motoyosi Sugita (杉田元宜)? Who is Motoyosi Sugita?

![Figure 1: Prof. Motoyosi Sugita. (Born August 1905—Died 14 January 1990). The picture was taken at the age of 79 in front of his second house, Hokuto-shi, Yamanashi, Japan in 1984. (by courtesy of Mrs. Setsu Honda).](image)

The name of Motoyosi Sugita (see Figure 1) is "widely unknown" all over the world today. It is so as well even in Japan nowadays. In this lecture, I would like to introduce you to this important Japanese theoretical physicist.

I did neither know his name nor his work until this spring in 2016. As I started recently writing a paper on the theory of thermodynamics in the irreversible processes, I found him, this brightest fellow in the early stage of Japan after WWII. Actually he was one of the top figures in the theoretical physicists in Japan right after WWII.
1.1. When and how did I know Motoyosi Sugita?

![Figure 2: My personal communications to know Motoyosi Sugita.](image)

Until recently I have neither known his name nor his work. By some accident I became aware of his name in Spring in 2016.
1.2. Birth

Motoyosi Sugita was born in Yatsushiro-machi in Kumamoto prefecture in Japan on August in 1905. Exact day of the born was not known so far. His father was Heishiro Sugita and his mother Haya Sugita.

They had the first boy, but the boy was gone by sick before Motoyosi was born. So, Motoyosi became the officially first son of their family.

His father Heishiro was the school teacher, later became a principal so that he went many places for teaching as a principal. During Heishiro was spending time at Kumamoto with his mother, Motoyosi was born.

1.3. Education

He graduated from the elementary school attached to the Kochi Teachers College and entered the Dai-ichi Junior High School in Kochi prefecture in 1919.

In 1921 he was admitted to the Konan Junior High School in Kobe, Hyogo Prefecture, moved from the Junior High School in Kochi. At this time most of good high schools in Japan had both junior high school and high school as one school system for 5–6 years. The Konan High School was one of them.

In 1926, he graduated from the physical science division in the Konan High School and entered the Department of Physics, the Faculty of Science, the Tokyo Imperial University.

In 1929, he graduated from the Department of Physics, the Faculty of Science, the Tokyo Imperial University.
1.4. Life and Working

In 1929, He was enrolled as a researcher at the Institute for Electricity (Denki-Shikenjo), the Ministry of Traffic and Postal Affairs (Teishin-sho).

In 1933, Motoyosi Sugita married Ms. Grace Sakae Oyama (see Figure 3). Grace is her Canadian name. She was a Japanese originated Canadian whose ancestry was Christian and immigrated from Hirosaki, Aomori, Japan. She was born in Vancouver, British Columbia, Canada. She graduated from the Victoria High School in Vancouver, Canada. She entered the Nursing School in Lamont, Alberta, Canada in 1928 and graduated at the top of the school. She became the first nurse of the Japanese-Canadians in Canada.

Figure 3: Prof. Motoyosi Sugita and his wife, Grace Sakae Sugita. The picture was taken at his age of 56 in front of her parents’ home in Hirosaki, Aomori, Japan in July, 1961, when they visited there for their greeting to the family right before they went to attend the Conferences in Canada and USA. During the visit abroad she was able to meet her family and relatives in Canada for the first time in 28 years since she came to Japan for her marriage with him. (by courtesy of Mrs. Setsu Honda).
In 1933, she came to Japan for marriage with Motoyosi Sugita, leaving her family in Canada. During WWII, she spent very sad time because Japan and Canada became enemy each other, and her family in Canada was forced to be sent to the concentration camps in Canada. Long after WWII, when they visited USA and Canada for attending the International conferences for biophysics and bioengineering, she was able to meet her family members in Canada for the first time in 28 years.

They had one son, Yūkiti. Yūkiti went to Indonesia for his business after Motoyosi and Sakae died. However, he failed his business and he returned back to Japan. He spent his final days in his family’s summer house in Hokuto-shi, Yamanashi, Japan. Yūkiti died on 2 August 2012. Only one relative of Motoyosi Sugita’s family is Mrs. Setsu Honda who lives in Hirosaki, Aomori, Japan. Other relatives are now living only in Canada.

Figure 4: Mrs. Setsu Honda with her husband and her relatives in Canada. Kate Keiko McCloskey (Oyama, 103 years old), her son Michel, and his daughter and her grand daughter Quinn. (by courtesy of Mrs. Setsu Honda).
In the last year of 2016, I found his last relative whose name is Mrs. Setsu Honda who lives in Hirosaki, Aomori under the assist of Mrs. Noriko Terui who lives in Ōtaniyama(大谷山), Hōjōji(宝城寺) of Sōtōshū(曹洞宗) in Saitama. The above information was sent as a letter from Mrs. Setsu Honda as her courtesy. I really appreciate it from the bottom of my heart.

In September, 1934, he became a teacher at the School for the Japanese Navy Organization.

Figure 5: Dr. Motoyosi Sugita The picture was taken at the age of 29 in front of his house in Tokyo, Japan in Summer in 1934. His son Yūkiti was born in May in this year. Yūkiti passed away on the 2nd of August in 2012. (by courtesy of Mrs. Setsu Honda).
In August, 1941, he retired the School for the Japanese Navy Organization and became a researcher in Kobayasi Institute in Tokyo.

Figure 6: Personnels of "Kobayasi Riken" in 1945. The picture was probably taken in front of the Kobayasi Institute (Kobayasi Rigaku Kenkyujo, shortly Kobayasi Riken), Tokyo, Japan, in March in 1945, right after WWII. Dr. Motoyosi Sugita is the second person from the left in the second row. (by courtesy of the Kobayasi Rigaku Kenkyujo).
In 1942, he published his first text book ”Thermodynamics New Lecture”.

He became a lecturer at the Department of Industrial Management, the Tokyo Commercial University.
In June, 1943, he published a book on the History of Physics.

In March, 1944, he became a professor at the Department of Industrial Management, the Tokyo Commercial University. In April he also worked as a lecturer at the Tsudajyuku University.
In June, 1949, he became a professor at the Department of Economics, the Hitotsubasi University (see Figure 9). As a concurrent post he became a professor at the Department of Commercial Science, the Hitotsubasi University (until it was repealed by the school system change by the Government in 1951).

Figure 9: Prof. Motoyosi Sugita. The picture was probably taken at the age of 74 in the home office of his house, Tokyo, Japan in 1979. (by courtesy of Misuzu Shobo).
In September, 1949, he earned the Ph.D. in Science from the Kyoto University by the doctoral thesis ”Thermodynamics of Transient Phenomena”, whose partial fulfilment was published as a book ”Thermodynamics of Transient Phenomena” from Iwanami-shoten in 1950.

Figure 10: Thermodynamics of Transient Phenomena. M. Sugita, (Iwanami, Tokyo, 1950). in Japanese. (by courtesy of Dr. Hiroaki Yamada).
In April, 1953, as concurrent posts, he became a professor at the Department of Sociology and at the Department of Economics, the Hitotsubashi University. At the same time, he was promoted to a lecturer for Condensed Matter Physics, the Department of Engineering, the Meiji University.

In September, 1956, he became a professor both for the Tokyo Commercial University and Hitotsubashi University until it was repealed by the school system change by the Government in 1962.

In April in 1959, he became a lecturer for the intensive lecture for Modern Technology at the Department of Management Science, the Konan University and a lecturer for the intensive lecture for the General Commercial Engineering, the Department of Economics, the Ooita University.

1.5. Visits abroad

In July, 1961, he visited the United States of America and Canada for three months. He attended the 4th International Conference on the Medical Electronics held at New York and the International Conference on Mathematical Biology held at North Carolina.

In August in 1965, he visited the U.S.S.R., Austria, Italy, France, England, West Germany, and Denmark for three months. He attended the International Conference on Molecular Biology held at Napoli, Italy and the second International Conference on Biometrics held at Helgoland, West Germany.
At the time, Motoyosi Sugita founded the Japanese Biophysics society as one of the first founding members. He became the president for Bioengineering of the Japanese Society for Medical and Biological Engineering (until 1967).

To start up the society, in order to show how the scientific society of Biophysics is important to the Japanese Government, they presented a book on Biophysics as the proceedings of the first meeting among the Japanese Biophysicists:

![Image of the book](image.png)

**Figure 12**: Physics Aspects of Life Phenomena. S. Oka, H. Kubo and M. Sugita, (Unoshoten, Tokyo, 1966). in Japanese. (by courtesy of Mrs. Noriko Terui).

In 1967, he visited the U.S.S.R., Sweden, West Germany, Netherlands, Belgium, France, Swiss, Austria for three months. He attended the 7th International Conference on Medical Electronics held at Stockholm, Sweden and the 3rd International Conference on Biometrics held at Helgoländ, West Germany.
In 1969, he retired from the Hitotsubasi University and became a professor emeritus (see Figure 13).

![Prof. Motoyosi Sugita](image)

**Figure 13:** Prof. Motoyosi Sugita. The picture was taken at his age of 80 in front of his second house in Hokuto-shi, Yamanashi, Japan in August in 1985. (by courtesy of Mrs. Setsu Honda).

On the 14th day of January in 1990, he passed away at the age of 85.
1.6. Scientific Publications

Motoyosi Sugita published many important scientific papers. Before WWII, he published papers written in German. After WWII, he published many papers in the Japanese science journals for the public such as *Kagaku* (meaning Science) and *Seibutsu Kagaku* (meaning Bioscience) and *Iryo Denshi to Seitai Kogaku* (meaning Medical Electronics and Bioengineering).

He published many Japanese articles in his working place reports: in the journal of Kobayasi Institute such as the Bulletin of Kobayasi Institute; and in his Hitotsubasi University journals such as the Annals of Hitotsubasi University, Hitotsubasi Ronso, the Bulletin of Hitotsubasi University.

He also published many papers written in English in Western Journals such as the Journal of Physical Society of Japan and the Journal of Theoretical Biology, as in the references.

And also he published many other papers on Physics education and Mathematics education as well, which are neither include nor listed in this paper. You can just see them in the National Diet Library, "Kokkai Toshokan" (国会図書館), of Japan.
1.7. Scientific Publications

At the same time, Motoyosi Sugita published many textbooks as well as the general books, which were all written in Japanese such as Physical Aspects of Life Phenomena, Research of Life, Society and Cybernetics, What is Cybernetics?, W. Heitler: Thinking and Wanderings, What is Information Science?, Society and Theory of Systems, Information Science, Bionics and Life Theory, Recommendation of Engineering Thinking, The Function of Academics and Creation.

Figure 14: M. Sugita’s books published from 1942 to 1979. in Japanese. Only the books that I have are shown.
1.8. The Research History of Motoyosi Sugita

As early as in 1930’s before WWII, he started to study physics. During this time, at first he seemed to spend much time to translate German physics papers written in Germany (Deutschland) such as Carl Wagner(1929) and Georg Siemens(1931) into the Japanese and published the articles to the Journal of the Mathematical and Physical Society of Japan (Su-butsu Gakkai Shi).

Once he found the concept of the virtual heat, he applied it to the thermodynamics of transient phenomena, and in doing so, he published papers in German in the Japanese journals(1932–1942).

Thus he seemed to be an expert for the German language in the Japanese physics society at that time before WWII.

Motoyosi Sugita studied the foundation of thermodynamics for biological systems(1942), and continued it after WWII. From the line of his German physics study which was the top physics country at that time mentioned above, he studied the theory of the German physicists, Becker and Döring(1935) and Volmer(1939) and an American physicist Frenkel(1939) on the cluster growth in the metastable phases in supersaturated vapors.

As early as in 1948 right after the damage of WWII slightly reduced in the society, Motoyosi Sugita published an important paper that discussed the relationship between the metastable(or quasi-static) phenomena in thermodynamics and biological phenomena in the Japanese journal, Kagaku(1948). It was also published in the textbook entitled by Thermodynamics of Transient Phenomena(1950).

As the Japanese society was coming back till 1950 he published a more fundamental paper in a Japanese journal, Seibutsu Kagaku(1950).

After a long study on the theory of thermodynamics in the transient phenomena such as life, he first postulated that

\[
\text{there might exist the 4th law of thermodynamics; otherwise one cannot understand biological phenomena.}
\]

He stated his considerations on it in §5 entitled by ”Can one consider the 4th law of thermodynamics?”.

I would like to quote here in the corresponding part from its English version(1951) as follows:
By the way, let us think here the circumstance deeply. According to the 2nd law of thermodynamics, Gibbs’ free energy, $G$, of the world has tendency to decrease in isothermal and isometric change. On the other hand, we find the tendency that the velocity of decreasing of $G$, i.e., $\dot{G}$ wants to take a large value as far as possible $\ddot{G}$.(1) This might be a general principle of nature which I should like to call temporarily the 4th law of thermodynamics.

The foundation of such a large principle will be discussed later, and we can suggest here that it is very important and beneficial idea that the nature of the transient phenomena as well as the living system may be clarified and explained uniformly by this principle.

There are many delicate problems concerning human thought if we propose to clarify the nature of life on the basis of physical and chemistry. In any way the matter looks like as if it were concerned in the 4th law. ⋯⋯⋯


⋯⋯⋯それはさておき、上の事情をつきつめると f.e. の $G$ が極小値にむかって減少して行く $\ddot{G}$ というのが熱力学の第 2 法則の主張であるように（実際には太陽からの光のエネルギーの補給がある間光合成が行われ、平衡状態の死相には幸いにして到達しないが）、$G$ の減少速度すなわち $|\dot{G}|$ ができるだけ大きい値をとろうとしている $\ddot{G}$ が大きいよう、私は便宜上仮にこれを熱力学の第 4 法則と呼ぶことにする。その証明というか基礎づけは後回しとして、生物現象をはじめ過渡的現象のいろいろの特色はこの法則によって都合よく説明できるという見込みを持っている。また生物現象の物理的化学的解釈は必ず思想的なものと衝突するか間接的（戦略的）に影響しあうかするが、その是非は別として、それは実は第 4 法則に関係することで、直接第 2 法則にはかかわらないことなのである。⋯⋯⋯

(1) 杉田元宜, 新しい生物学, (日本科学社, 1949) の中小論.
Hence, following the line of thought of Motoyosi Sugita (1950), I can summarize the laws of thermodynamics as follows:

(i) The 1st law (W. Thomson’s principle):
The Gibbs free energy $G$ is conserved in a closed system; $\dot{G} = 0$.

(ii) The 2nd law (Clausius’s principle):
The entropy $S$ always increases in any process; $\dot{S} = -T \dot{S} \leq 0$.

(iii) The 3rd law (Nernst’s theorem):
The entropy approaches zero as the absolute temperature $T$ approaches zero; $S(T = 0) = 0$.

(iv) The 4th law (M. Sugita’s postulate):
The decreasing rate of the Gibbs free energy always takes the maximum in any process; $|\dot{G}| = \text{max}$, where $\dot{G} \equiv -|\dot{G}| \leq 0$. 

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Fortunately Sugita published the above paper one year later in English (1951). But it was unfortunate since the journal of the Hitotsubasi university (to which he belonged) that he published was not famous at all among Western physicists as well as the Japanese physicists. And also it has not been available to the public for so long until recently after the internet service was provide.

In 1953 Motoyosi Sugita has found the way to apply the theory of thermodynamics of transient phenomena to more realistic biosystems such as metabolic systems (1953–1955).

From this stage his research entered the second stage to construct the thermodynamics of life. Step by step his way of thinking became cybernetics-like, where the feedback control systems played an important role in his theory (1955–1968).

Since no computer system was easily available for the bio-systematic calculations in Japan at that time, Motoyosi Sugita collaborated with electrical engineers to construct analog-digital computer circuits for their calculations. They simulated the circuits to obtain the solutions of their own models of the metabolic control systems. These ideas were summarized as books (1966, 1970, 1979).


Although he published many papers and textbooks, he published only about ten papers in English by unknown reasons. That is why he was so unknown in the Western countries as well as in Japan. Hence, nobody knew him nowadays, and so did I, in spite of his extremely important contributions to the thermodynamics theory.

In this lecture I would like to review some important consequences of his theory and discuss the maximum principle in the open non-equilibrium systems as the foundation for the 4th law of thermodynamics to the readers especially in the Western countries.
2. The Bright Ideas of Motoyosi Sugita

The most important concepts created by Motoyosi Sugita are probably the concepts in thermodynamics in order to describe the irreversible changes in thermodynamics of transient phenomena:
(1) the broad quasi-static change
(2) the virtual heat
(3) the irreversible cyclic processes.

2.1. The Broad Quasi-static Change

The broad quasi-static change is defined as:

\begin{align}
    (i) & \quad P = f_1(V, T), \quad (ii) \quad U = f_2(V, T), \\
    & \quad \text{where } f_1 \text{ and } f_2 \text{ are some functions of } V \text{ and } T, \text{ respectively as a generalization from those for an ideal gas where } P = kT/V \text{ and } U = \frac{3}{2}kT, k \text{ being the Boltzmann constant.}
\end{align}

This means that (a) the process is indefinitely very slow; (b) the local equilibrium can be satisfied even in the non-equilibrium states, where the broad quasi-static change makes sense. When these conditions are assumed to be satisfied, one can almost follow the standard approach of the quasi-static processes in thermodynamics. The concept of the broad quasi-static change has the amazing possibility of development, once it is combined to statistical mechanics.

Suppose that many macroscopic parts are in the equilibrium state. Let us denote by $S_i$ the entropy of that $i$-th small part and by $F_i$ its Helmholtz free energy. The values of the entropy $S$ and the Helmholtz free energy $F$ of the whole system are given by

\begin{align}
    S &= \sum_i S_i, \quad F = \sum_i F_i. \\
    S_i &= k \ln W_i, \quad F_i = -kT \ln Z_i. \\
    W &= e^{S/k} = \prod_i W_i, \quad Z = e^{-F/kT} = \prod_i Z_i.
\end{align}

This means that when one considers the broad quasi-static change, one should not take or need not take the $W$ or $Z$ over the entire phase space. One must cut off the phase space into the small pieces that are in local equilibrium, and concatenate them to cover the whole phase space.
2.2. The Virtual Heat

The virtual heat is defined as follows:

\( \delta Q_e \) = the heat ejected from the reservoir that is outside the system.
\( \delta Q \) = the heat absorbed by the thermodynamic system.
\( T \) = the temperature of the system.

Suppose that the reservoir follows the same change of the broad quasi-static change as the system under consideration. Assume that the origin of the irreversibility lies inside the system and consider the friction inside the system.

\( dW \) = the work to do the outside system (= \( PdV \) for the piston-cylinder system).
\( fdV \) = the work consumed by the friction = the virtual heat.

Then, we have

\[
dU + dW = \delta Q_e, \tag{2.A}
dW = PdV - fdV. \tag{2.5}
\]

Substituting Eq.(2.5) into Eq.(2.A), we obtain

\[
dU + PdV = \delta Q_e + fdV. \tag{2.6}
\]

Therefore,

\[
\delta Q = \delta Q_e + fdV, \tag{2.7}
dU + PdV = \delta Q. \tag{2.B}
\]

Now, from the concept of the broad quasi-static change, \( \delta Q \) must have the integration denominator as

\[
\frac{dU + PdV}{T} = \frac{\delta Q}{T} = dS. \tag{2.8}
\]

Here we never think as if

\[
\delta Q_e = TdS \tag{2.9}
\]

holds true.

If we think of the adiabatic change without input and output of heat, i.e., \( \delta Q_e = 0 \), then

\[
dU + PdV = \delta Q = fdV. \tag{2.10}
\]
Hence,

\[ dS = \frac{dU + PdV}{T} = \frac{fdV}{T} > 0. \]  \hspace{1cm} (2.11)

In Eq.(2.5), if the work \( fdV \) is consumed and become the heat outside of the cylinder, then for the inside of the system (e.g., the gas)

\[ dU + PdV = \delta Q_e = \delta Q = TdS. \]  \hspace{1cm} (2.12)

For the outside of the system, the reservoir gives the heat \( dQ_e \) to the gas system and at the same time it receives as a heat the energy lost from the system by the work \( fdV \). Hence,

\[ dQ_e = -\delta Q_e + fdV = TdS_e \]  \hspace{1cm} (2.13)

Therefore, for the whole system we have

\[ dS + dS_e = \frac{fdV}{T} > 0. \]  \hspace{1cm} (2.14)

**2.3. The Irreversible Cycle**

Let us consider the process when the irreversible cyclic process is preformed. 
\( T_0 \) = the lowest possible temperature available of the thermal reservoir. 
\( dS_e \) = the entropy change of the reservoir with temperature \( T_e \). 
\( \Delta Q_e \) = its lost heat.

Then

\[ dS_e = -\frac{\Delta Q_e}{T_e}, \]  \hspace{1cm} (2.15)

since the reservoir gives the heat \( \Delta Q_e \) to the system. 
\( T \) = the temperature 
\( S \) = the entropy of the system (working material) that performs the cycle.

Then we have

\[ dS = \frac{\Delta Q_e + \Delta H}{T}, \]  \hspace{1cm} (2.16)

since the system receives the heat \( \Delta Q_e \) in addition to the virtual heat \( \Delta H \) of the process, where \( T < T_e \).
Hence, for the whole system, we have
\[ dS_e + dS = \Delta Q_e \left( \frac{1}{T} - \frac{1}{T_e} \right) + \frac{\Delta H}{T} > 0. \] (2.17)

After finishing the cyclic process, the system has to come back to the initial stage of the process (i.e., the initial condition) such that it yields
\[ \oint dS = 0. \] (2.18)

Hence, the total entropy change in the cycle is given by
\[ \Delta S = \oint dS_e = \oint \left( \frac{1}{T} - \frac{1}{T_e} \right) \Delta Q_e + \oint \frac{\Delta H}{T} > 0. \] (2.19)

On the other hand, for reversible processes, since
\[ T = T_e, \quad \delta Q = \delta Q_e, \] (2.20)
on one has
\[ \oint dS = \oint \frac{dQ}{T} = 0. \] (2.21)

Thus, the entropy change occurs only in the thermal reservoir outside the system in the process of the irreversible cycle.

3. The Diffusion Phenomena

The diffusion phenomena are really important phenomena when we construct the theory of thermodynamics in transient phenomena. In order to see how the concepts of the broad quasi-static change and the virtual heat work in each physical problem, Motoyosi Sugita applied them to the diffusion problem in his test book (1950). To do so, I would like to follow his argument.

3.1. Langevin Equation

Consider an ideal gas that is constructed from the mixing of the two species of molecules 1 and 2. For the sake of simplicity, we assume that the density gradient only exists in \( x \) direction. This is equivalent to consider the one-dimensional diffusion problem along \( x \) direction.
\[ m_1(m_2) = \text{the mass of each molecule of species 1 (species 2).} \]
\[ n_{1i}/cm^3 \ (n_{2i}/cm^3) = \text{the number of molecules per } cm^3 \text{ of species 1 (species 2).} \]
\[ v_{1i}(v_{2i}) = \text{the velocity along } x \text{ direction.} \]

The mass of species 1 that passes the interface of 1 cm\(^3\) piercing \(x\) in a second is
\[
J_1 = \sum_i n_{1i}m_1v_{1i} = m_1 \left( \sum_i n_{1i} \right) v_i. \tag{3.1}
\]

Hence,
\[
v_i = \frac{\sum_i n_{1i}v_{1i}}{\sum_i n_{1i}}. \tag{3.2}
\]

\(n'_1, n'_2\) = the mole numbers per \(cm^3\) of molecules of species 1 and 2.

We have
\[
\begin{align*}
N_a n'_1 &= \sum_i n_{1i}, \\
N_a n'_2 &= \sum_i n_{2i}, \\
N_a m_1 &= M_1, \\
N_a m_2 &= M_1,
\end{align*}
\tag{3.3}
\]
where \(N_a = 6.06 \times 10^{23}\), the Avogadro number.

We now have
\[
J_1 = m_1 N_a n'_1 v_1 = M_1 n'_1 v_1. \tag{3.1'}
\]

Or if we use \(n' = n'_1 + n'_2\), \(c_1 = \frac{n'_1}{n'}\), \(c_2 = \frac{n'_2}{n'}\), then
\[
J_1 = M_1 n' c_1 v_1. \tag{3.1''}
\]

Now taking as \(m_1 \approx m_2\) and if one can ignore the shift of the center of gravity due to the diffusion, then from Fick’s law, one can obtain
\[
J_i = n'M_i c_i v_i = -D_i \frac{\partial c_i}{\partial x}, \tag{3.4}
\]
where \(i = 1, 2\).

On the other hand, if it cannot be ignored then one has to put the viscous term of the fluid. If we put as
\[
K_i = n'M_i k \frac{T}{D_i}, \tag{3.5}
\]
then the above equation looks like the Langevin equation type such as

\[ K_i v_i = -kT \frac{\partial \log c_i}{\partial x}. \]  

(3.6)

So far we have considered the case of ideal gases. However, for more general cases, if we use

\[ \mu_i = \mu_{i0} + kT \log c_i, \]  

(3.7)

the right hand side of Eq.(3.6) can be rewritten as

\[ K_i v_i = -\frac{\partial \mu_i}{\partial x}, \]  

(3.6’)

or if we use \( J_i \) then we can rewrite as

\[ J_i = \frac{n’M_i c_i \partial \mu_i}{K_i \partial x}. \]  

(3.4’)

As Sugita pointed out, the Langevin equation is the equation of motion that one thinks as if the stationary motion is considered statistically so that the effect of acceleration cannot play a role to the averaged velocity, and the ”random forces” come from like-particles in thermal motions are statistically averaged.

Next let us explain that when the work done by the resistance of friction \( K_i v_i \) is added to the system as the virtual heat, the increase of entropy by this process becomes that of entropy by the mixing of the molecules of species 1 and 2.

3.2. Mixing Entropy and Free Energy

Now let us denote by \( c_i(x) \) the density of the molecule of species \( i \) at each point \( x \) in the midst of the mixing process. And let us denote by \( n_i(x) \) the number of the molecule of species \( i \) at each point \( x \) in the midst of the mixing process such that \( c_i(x) = n_i(x)/N \), where \( N = \sum_i n_i(x) \). Assume that the chemical potential (per mol) for each component of \( i \), \( \mu_i(x) \), is given as

\[ \mu_i(x) = \mu_{i0} + RT \log c_i(x), \quad (i = 1, 2), \]  

(3.8)

where \( \mu_{i0} \) is assumed to be constant in the system and \( R = N_a k \). Then, the Gibbs free energy of the entire system should be given as

\[ G = \sum_i \int \mu_i(x)n_i(x)dx, \quad (i = 1, 2). \]  

(3.9)
If the equation is reversely seen, then the chemical potential has to be defined by

$$
\mu_i(x) = \frac{\partial G}{\partial (n_i(x)dx)}, \quad (i = 1, 2). \tag{3.10}
$$

Now, since the $G$ is decreasing by the mixing, from Eq.(3.9) we have

$$
G = \sum_i \int \mu_i(x)n_i(x)dx < 0, \quad (i = 1, 2). \tag{3.11}
$$

This means that in the mixing system of ideal gases, the mixing entropy is increasing by the mixing of the molecules and by it $G$ is decreasing. And although the decrease of $G$ is the decrease per second in the irreversible process, we cannot necessarily know but surely know the change in time of $G$ in the midst of the process.

Based on the Langevin equation Eq.(3.6'), suppose that the molecule is forced to move by $-\text{grad} \mu_i(x)$ and it transports against the friction. Suppose that we can regard the friction the virtual heat and therefore the entropy of the system can increase by the virtual heat.

For the sake of simplicity let us limit ourselves to the ideal gases. Then, only the energy per molecule $K_i v_i^2$ is given as a heat per second from the virtual heat. This amount of the quantity per volume becomes $\bar{n}_i K_i v_i^2$. For the whole system it provides only the heat that is defined by

$$
\sum_i \int \bar{n}_i K_i v_i^2 dx = n' \sum_i \int c_i K_i v_i^2 dx. \tag{3.12}
$$

If we assume the process is an isothermal change, then replace $K_i v_i$ by Eq.(3.6'). We have

$$
\Delta S = -\frac{n'}{T} \sum_i \int c_i v_i \frac{\partial \mu_i(x)}{\partial x} dx
$$

$$
= -\sum_i \int \frac{J_i}{TM_i} \frac{\partial \mu_i(x)}{\partial x} dx
$$

$$
= -\frac{1}{T} \sum_i \int \frac{\partial}{\partial x} \left( \frac{J_i}{M_i} \mu_i(x) \right) dx + \frac{1}{T} \sum_i \int \frac{\mu_i(x)}{M_i} \frac{\partial J_i(x)}{\partial x} \tag{3.13}
$$
The first term in the right hand side vanishes if the boundary condition is taken. In the second term in the right hand side, since we have the continuity equation:

\[
\frac{\partial M_i n_i(x)}{\partial t} = - \frac{\partial J_i(x)}{\partial x},
\]

(3.14)

if we change \( n'_i \) as \( n_i \) in Eq.(3.1'), then Eq.(3.13) can be represented as

\[
\Delta S = -\frac{1}{T} \sum_i \int \mu_i(x) \dot{n}_i(x) dx.
\]

(3.15)

On the other hand, in the ideal system the change in \( G \) only occurs in the change of entropy. Therefore, if we rewrite \( \Delta S \) as \( \dot{S} \), then we obtain

\[
\dot{G} = -T \dot{S} = \sum_i \int \mu_i(x) \dot{n}_i(x) dx.
\]

(3.16)

Hence, this agrees with Eq.(3.11). From considering the above situation, we can recognize that the assumption that the force acting on the diffusion particle is given by Eq.(3.6') is not inconvenient.

Let us consider the case of the non-ideal systems. In this case the chemical potential \( \mu_{i0} \) becomes density dependent. And in the case of the isothermal and isobaric mixing, the volume change and the flow in and out of the heat can occur. And therefore the entropy change is no longer given by that of the ideal mixing, \( R \sum_i n_i \log c_i \). For this time, Eq.(3.9) and Eq.(3.11) hold true and the entropy increase due to the receive of the virtual heat is given by Eq.(3.15) as well. How can one interpret this? The mixing entropy in this case can change since there occurs the thermal heat exchange other than the virtual heat. If temperature \( T \) and pressure \( P \) are kept constant, and if the work done for the outside of the system is given by \( PdV \) and the change in the internal energy is given by \( dU \), then the input and output of the heat is given by

\[
\delta Q_e = dU + PdV.
\]

(3.17)

Therefore, once we add the heats due to Eq.(3.15) and Eq.(3.16) to the above increase of entropy due to \( \delta Q_e \), we find

\[
\dot{S} = \frac{\dot{U} + P\dot{V}}{T} - \frac{1}{T} \sum_i \int \mu_i(x) \dot{n}_i(x) dx = \frac{\dot{U} + P\dot{V} - \dot{G}}{T}.
\]

(3.18)
This is not inconsistency but rather everything is consistent very much. If we compare the above with Eq.(3.16), then

\[ \dot{G} = -T\dot{S} + \dot{U} + \dot{PV} = -T\Delta S = \sum_i \int \mu_i(x)\dot{n}_i(x)dx. \] (3.19)

This means that \( \dot{G} \) occurs by \( \Delta S \) (\( \equiv \dot{S} \)). Thus, even for this case of non-ideal gases the entropy increase due to the friction by the mixing can be regarded as the heat received from the virtual heat source. This is also thermodynamical support for the phenomenological construction of the theory where the quantity such as \( \text{grad} \mu_i \) can be regarded as a ”field”. Motoyosi Sugita called this approach the \textit{Onsager-Meixner-Sugita’s method}(1950).

3.3. How to Count the Number of Partition

For this title, Motoyosi Sugita used the word the \textit{number of complexion}. The number of complexion is nothing more than the number of partition in classical statistical mechanics or the number of states in quantum statistical mechanics in the modern terminology.

When the system is in equilibrium, the number of ways that particles interchange their positions in the system is nothing but the number of complexion in his terminology. In this equilibrium case, one can definitely define the chemical potential such as Eq.(3.8).

Can such a treatment be allowed even in the midst of the non-equilibrium process?

This was the Motoyosi Sugita’s problem. Obviously, it is allowed for the equilibrium state of the process. But it is not trivial for the non-equilibrium state in the irreversible or transient phenomena.

Suppose that the previous argument that provides Eq.(3.8) is correct(1949). Assume that \( \mu_{i0} \) is constant. Then one finds

\[ G = \sum_i \int \mu_i(x)n_i(x)dx \]

\[ = \sum_i \int \mu_{i0}n_i(x)dx + RT \sum_i \int n_i(x)\log c_i(x)dx, \] (3.20)

where \( R = N_a k \), the gas constant and \( N_a \) the Avogadro number. Or regarding the above integral for \( dx \) as the sum over \( \Delta x \), we can rewrite it as in a different
form:
\[ G = \sum_i \sum_{\Delta x} \mu_i(x) n_i(x) \Delta x \]

\[ = \sum_i \sum_{\Delta x} \mu_{i0} n_i \Delta x + RT \sum_i \sum_{\Delta x} n_i(x) \log c_i(x) \Delta x. \quad (3.21) \]

Hence, by taking the functional derivative for the above with respect to \( n_i(x) \Delta x \), the chemical potential \( \mu_i(x) \) is given by

\[ \mu_i(x) = \frac{\partial G}{\partial [n_i(x)\Delta x]} = \mu_{i0} + RT \log c_i(x). \quad (3.22) \]

The second term in the right hand side comes from the mixing entropy of the system. Therefore, it corresponds to what one assumes that the number of partition at an instantaneous time in the midst of the process is given by

\[ W = \prod_j W_j = \prod_j \frac{[n_1(x_j)\Delta x_j + n_2(x_j)\Delta x_j]!}{[n_1(x_j)\Delta x_j]! [n_2(x_j)\Delta x_j]!}. \quad (3.23) \]

If we take \( S = k \log W \), then since

\[ G = \int \{ \mu_1(x)n_1(x) + \mu_2(x)n_2(x) \} dx = U + PV - TS, \]

\[ U = \int \{ \mu_{10}n_1(x) + \mu_{20}n_2(x) \} dx, \]

Eq.(3.22) is derived directly. Therefore, the meaning of \( W_i \) is the partition number that is considered within the local part of \( \Delta x_i \).

4. The Theory of Chemical Reactions

4.1. Chemical reactions

Chemical reaction:

\[ a_1 A_1 + a_2 A_2 + \cdots \rightarrow b_1 B_1 + b_2 B_2 + \cdots, \quad (4.1) \]

where \( A_i \) (\( B_j \)) stand for the reacting (produced) molecules and \( a_i \) (\( b_j \)) are positive integers representing stoichiometry of the reaction.
Motoyosi Sugita (1950, 1951) frequently used the following expression:

\[ \sum_{i} \nu_i A_i \rightarrow \sum_{j} \nu_j A_j, \quad (4.2) \]

where \( A_i \) (\( A_j \)) stand for the reacting (produced) molecules and \( \nu_i \) (\( \nu_j \)) are positive integers representing stoichiometry of the reaction.

\( N_i \) (\( N_j \)) = the number of reacting (produced) molecules of \( i \)th (\( j \)th) species in mole.

\[ c_i \equiv [A_i] = \frac{N_i}{N}, c_j \equiv [A_j] = \frac{N_j}{N} \]

where \( N = \sum_i N_i + \sum_j N_j \).

The changes in mole numbers of the reacting and produced molecules:

\[ \frac{dN_i}{\nu_i} = \frac{dN_j}{\nu_j} = \Delta n, \quad (4.3) \]

where \( i \) and \( j \) stand for the reacting and produced molecules.

The Gibbs free energy \( G \):

\[ G \equiv \sum_k \mu_k N_k, \quad (4.4) \]

where \( N_k \) and \( \mu_k \) are the number and the chemical potential of the molecule \( A_k \), respectively, and \( k \supset i, j \).

Equivalently,

\[ \mu_k \equiv \frac{\partial G}{\partial N_k}. \quad (4.5) \]

It means that if the amount of \( \Delta N_k \) of the \( k \)th molecules is added to the system from outside, then the work of

\[ \Delta G = \mu_k \Delta N_k \quad (4.6) \]

is done such that the Gibbs free energy increases.

Since the sum in the Gibbs free energy \( G \) is linear in \( N_i \), it shows a homogeneous equation. Hence, we have

\[ dG = \sum_k \mu_k dN_k. \quad (4.7) \]

Using the reaction equation of Eq.(4.3), we have

\[ \Delta N_i = -\nu_i \Delta n, \quad \Delta N_j = \nu_j \Delta n, \quad (4.8) \]
where if $\Delta n > 0$ then the reaction moves from the left to the right.

Substituting Eq. (5.9) into Eq. (5.8), we can derive the following:

$$\Delta G = - \left[ \sum_i \nu_i \mu_i - \sum_j \nu_j \mu_j \right] \Delta n = -\Delta \mu \Delta n,$$

(4.9)

where $\Delta \mu$ is defined by

$$\Delta \mu \equiv \sum_i \nu_i \mu_i - \sum_j \nu_j \mu_j.$$  

(4.10)

This is nothing but the Affinity introduced by De Donder (1936) and Progogine (1971) before WWII as well as Marcelin (1914) and Jouguet (1926) even before WWI in Western countries.

From the knowledge of thermodynamics, $G$ becomes the minimum when the system goes to chemical equilibrium. Hence, in chemical equilibrium, $G = \text{min}$; in other words $\delta G = 0$. Therefore, if we regard $\Delta G$ as a variation, then we find

$$\Delta G \geq 0.$$ 

(4.11)

This yields the following criterion for the direction of the reaction Eq. (4.2):

$$\begin{aligned}
\Delta \mu > 0 & \implies \text{left } \rightarrow \text{ right,} \\
\Delta \mu = 0 & \implies \text{chemical equilibrium,} \\
\Delta \mu < 0 & \implies \text{left } \leftarrow \text{ right.}
\end{aligned}$$

(4.12)

This is the criterion given through the concept of affinity.

The Gibbs free energy $G$ can be written as

$$G = \sum_k \mu_k N_k - TS_M.$$ 

(4.13)

Simply suppose that the mixing entropy is approximately given as

$$S_M = -R \sum_k N_k \log c_k,$$

(4.14)

Substituting Eq. (4.14) into Eq. (4.13), the chemical potential $\mu_k$ is given by

$$\mu_k = \mu_{k0} + RT \log c_k.$$ 

(4.15)
Substituting these into $\Delta \mu = 0$ in Eq.(4.10), we obtain
\[
\sum_i \nu_i u_{i0} + RT \log \prod_i c_i^{\nu_i} = \sum_j \nu_j u_{j0} + RT \log \prod_j c_j^{\nu_j}.
\]
(4.16)

This yields
\[
RT \log \left[ \frac{\prod_i c_i^{\nu_i}}{\prod_j c_j^{\nu_j}} \right] = \Delta \mu_0,
\]
where we have defined as
\[
\Delta \mu_0 \equiv \sum_i \nu_i u_{i0} - \sum_j \nu_j u_{j0}.
\]
(4.17)

Rewriting Eq.(4.17), the law of mass action in the chemical equilibrium is given by
\[
\frac{\prod_i c_i^{\nu_i}}{\prod_j c_j^{\nu_j}} = K(T) = e^{\frac{\Delta \mu_0}{RT}},
\]
(4.19)
where $K(T)$ is called the equilibrium constant at temperature $T$.

Now let us consider when the system is not in equilibrium. In this case, Eq.(4.2) yields the rate equation:
\[
\frac{dn}{dt} = k_f \prod_i c_i^{\nu_i} - k_b \prod_j c_j^{\nu_j},
\]
(4.20)

The relationship between $k_f$, $k_b$ and $K$:
\[
\frac{k_f}{k_b} = K(T).
\]
(4.21)

Here if we may follow the argument of Prigogine et al(1971,1999), then we may define as
\[
\frac{d\xi}{dt} = R_f - R_b,
\]
(4.22)
where
\[
R_f = k_f \prod_i c_i^{\nu_i}, \quad R_b = k_b \prod_j c_j^{\nu_j}.
\]
(4.23)

4.2. The Concept of the Generalized Nonlinear Ohm’s Law
Following the theory of Motoyosi Sugita (1970), let us define the chemical resistance \( R_c \) to the chemical reaction by

\[
\frac{1}{R_c} = k_f e^{-\frac{\sum \nu_i \mu_i}{RT}} = k_b e^{-\frac{\sum \nu_j \mu_j}{RT}} .
\]

(4.24)

The meaning is the detailed balance:

If we rewrite as

\[
k_f \equiv P_{i \rightarrow j}, \quad k_b \equiv P_{j \rightarrow i},
\]

\[
P_i = e^{-\frac{\sum \nu_i \mu_i}{RT}}, \quad P_j = e^{-\frac{\sum \nu_j \mu_j}{RT}},
\]

(4.25)

\[
\frac{1}{R_c} = P_i P_{i \rightarrow j} = P_j P_{j \rightarrow i} .
\]

(4.26)

Thus, the equation for \( R_c \) [Eq.(4.24)] indicates a kind of the detailed balance equation.

Motoyosi Sugita assumed:

\[
c_k = e^{\frac{\mu_k - \mu_{k0}}{RT}} .
\]

(4.27)

Using Eq.(4.27) together with Eq.(4.24), he was able to rewrite Eq.(4.23) as follows:

\[
R_f = k_f \prod_i c_i^{\nu_i} = e^{\frac{\sum \nu_i \mu_i}{RT}} k_f e^{-\frac{\sum \nu_i \mu_i}{RT}} = \frac{1}{R_c} e^{\frac{\sum \nu_i \mu_i}{RT}}
\]

(4.28)

\[
R_b = k_b \prod_i c_i^{\nu_i} = e^{\frac{\sum \nu_j \mu_j}{RT}} k_b e^{-\frac{\sum \nu_j \mu_j}{RT}} = \frac{1}{R_c} e^{\frac{\sum \nu_j \mu_j}{RT}}
\]

(4.29)

Applying these into Eq.(4.20) or Eq.(4.22) and rewriting \( J = \frac{dn}{dt} \),

\[
J = \frac{dn}{dt} = \frac{1}{R_c} \left\{ e^{\frac{\sum \nu_i \mu_i}{RT}} - e^{\frac{\sum \nu_j \mu_j}{RT}} \right\} .
\]

(4.30)

This expression has the generalized nonlinear form of the Ohm’s law:

\[
J = \frac{dn}{dt} = \frac{1}{R_c RT} \left\{ \sum_i \nu_i \mu_i - \sum_j \nu_j \mu_j \right\} .
\]

(4.31)

Now we are able to know the following relation:

\[
\Delta \mu \lesssim 0 \quad \iff \quad J \gtrless 0,
\]

(4.32)
Thus we can have the same criterion as that in Eq.(4.12) by considering Eq.(4.31):

\[
\begin{align*}
J > 0 & \implies \text{left } \rightarrow \text{ right,} \\
J = 0 & \implies \text{chemical equilibrium,} \\
J < 0 & \implies \text{left } \leftarrow \text{ right}
\end{align*}
\]

(4.33)

4.3. The Concept of the Field of Chemical Potential

Eq.(4.30) was first introduced by Motoyosi Sugita long long time ago (1948, 1950, 1951).

Becker and Döring(1935), Volmer(1939) and Frenke(1939)(shortly represent BDVF). They studied the theory of condensation considering the nucleation of clusters \(n\) in the supersaturated state. Therefore, it describes the non-equilibrium state in the irreversible process of condensation:

\[
(1) \rightarrow (2) \rightarrow \cdots \rightarrow (n) \rightarrow .
\]

(4.34)

Here in between the nearest states of clusters \((n-1)\) and \((n)\) E:

\[
J_{n-1,n} = \frac{1}{R_{n-1,n}^c} \left\{ e^{\frac{\mu_{n-1} + \mu_g}{kT}} - e^{\frac{\mu_n}{kT}} \right\}.
\]

(4.35)

Motoyosi Sugita recognized that when chemical equilibrium is slightly broken or when chemical reactions are going on, the physical conditions in chemical reactions are the same as those in condensation as well as nucleation.

\[
J(\text{BDVF}) = \frac{1}{R_c} \left\{ e^{\frac{\mu_{n} + \mu_g}{kT}} - e^{\frac{\mu_{n+1}}{kT}} \right\}
\]

\[
\downarrow
\]

(4.36)

\[
J(\text{Sugita}) = \frac{1}{R_c} \left\{ e^{\frac{\sum_i v_i \mu_i}{kT}} - e^{\frac{\sum_j \mu_j}{kT}} \right\}.
\]

In my opinion, it is obvious that his way of thought came from this experience in his physics study, and then he applied the concept to other physical and chemical examples such as chemical reactions.

The first look of Motoyosi Sugita for this discovery seems to be the following simple equation:

\[
\mu_i(x) = \mu_{i0} + \phi_i(x) + kT \log c_i(x),
\]

(4.37)
where $\phi_i(x)$ means the electric potential acting on the molecule of species $i$ and others are the same as before [Onsager(1931), Debye–Hückel(1923) and Onsager–Samaras(1934)].

Then he extended his way of thinking so that even if no electric potential exist, then the chemical potential as a field is meaningful.

Why not for other systems? What’s wrong with this?

So, Motoyosi Sugita stepped forward to go beyond the equilibrium thermodynamics to the quasi thermodynamics of transient phenomena.

Thus, although we think of chemical potential such as a numerical value for the equilibrium state in the standard point of view of thermodynamics, Motoyosi Sugita never thought like this but he always thought that chemical potential is a field defined on space-time such as the field in field theory even for dynamic, nonuniform, irreversible, non-reproducible and transient phenomena. This is his philosophy on the field of chemical potential.

4.4. Cooperative Phenomena and Chemical Potential

4.5. The Concept of Invisible Force, the $\mu$-field

5. The Maximum Principle in Transient Phenomena

5.1. $|\dot{G}| =$Max Conjecture and the 4th Law of Thermodynamics

Motoyosi Sugita wrote a paper entitled in Japanese, ”Biological Thermodynamics and its Method” (1950)[”Thermodynamical Method in Biology” (1951), the Annals of the Hitotsubasi University]. He stated in Japanese on the existence of the 4th law of thermodynamics (1950) as the paragraph quoted in Introduction. And also he first applied his theory of thermodynamics in the transient phenomena to the theory of metabolism.

For the reason why Motoyosi Sugita believed the existence of the 4th law of thermodynamics, he listed several examples that seem to be related to this 4th law as follows:

Here let us see many instances suggesting this large principle of thermodynamics.

(i) The cascade principle(Stufenregel) found by W. Ostwald(1939) shows that the nature has the tendencies as if it wanted to take the
pass of smaller resistance or make a de tour and want to establish
the equilibrium as fast as possible.

(ii) Generalizing further the rule described above, it might be
said that the nature prefers the line of the least resistance, if there
are ways side by side for the equilibrium.

(a) According to Volmer(1939), for instance, the crystal forma-
tion shows that such a pass is taken actually.

(b) Eyring(1935) and others(1941) called such a process rate
determining.

(c) Electric current in conductor takes the distribution that heat
loss is minimum if the total current takes a given value. Therefore
the heat generation must be maximum if the potential difference
will be taken as constant. Therefore, if a cell is applied to drive the
current, it will take the distribution to dissipate the free energy of
the cell as fast as possible.

(d) Onsager(1931) has derived his reciprocal relation from the
principle of least dissipation function. This principle might be con-
sidered to the maximum velocity of entropy increase which will be
discussed later.

(iii) If a new passage is built independently which has less re-
sistance than others already existing, then the circumstance above
described, that might be the 4th law of thermodynamics, may also
be seen from our common sense.

(a) The new way may be considered having delicate catalytic
action, therefore, large free energy of activation or small entropy.
The free energy of activation determines the rate of development of
such a passage acting as if the initial cost is to construct a high-
way. That is why the construction of the way of small resistance
is retarded. Nevertheless, it becomes rate determining when it is
performed and the old ways become only bypass or will be ruined.

(b) The idea of natural selection or struggle for life of biology
may be considered as having the relation to this principle. That is
the free energy discharged through the old passage is used to the free
energy of activation of new way, and the material itself constituting
the old way may be useful also as the material of construction (see
(c) Such a circumstance like natural selection can be seen also in the inorganic worlds. For instance, let us observe the nuclear formation of ice in supersaturated water vapor under freezing point, and containing super-cooled water droplets. If the crystal nucleus is formed, not only the condensation occurs on this nucleus, but the super-cooled droplets vaporize and disappear. This is the consequence of the 4th law and the same phenomena can be seen on the discharged plate of PbSO$_4$ of battery and also in the case of recrystallization of metals and others, and they are playing a role to promote the tendency to the thermodynamic equilibrium.

Thus from the early beginning of his research he recognized and imagined the existence of the 4th law of thermodynamics, where he expected that some kind of the generalization of the least dissipation of energy of Onsager could be necessary. Therefore, I would like to call his expectation the Motoyosi Sugita’s $|\dot{G}|=\text{max}$ conjecture.

In the next section of that paper (1950, 1951), ”VI. Mathematical Theory and Conclusion”, he sketched the outline of the 4th law of thermodynamics as follows:

(i) First, on the base of microscopic reversibility, Onsager (1931) has shown that $\Delta(\dot{S} - \Phi) \geq 0$. Exactly speaking, it is given by

$$
\delta(\dot{S} - \Phi) = 0, \text{ equivalently } \dot{S} - \Phi = \text{Max}, \quad (5.1)
$$

where $\dot{S}$ is the velocity of entropy increase of the total system and $\Phi$ is the Rayleigh’s dissipation function.

(ii) On the same base as Onsager, Landau and Lifshitz (1959) have shown that

$$
\dot{G} = -2\phi, \quad (5.2)
$$

where $\phi = T\Phi$.

(iii) Let us denote by $N_k$ the parameter expressing the transient state, and let us assume that $G$ is expressed by $N_k$ using the cut off method, then

$$
\dot{G} = \sum_k \mu_k \dot{N}_k, \quad (5.3)
$$
\[ \mu_k = \frac{\partial G}{\partial N_k} = \mu_{k0} + kT \log c_k, \quad c_k = \frac{N_k}{N} \]  

(5.4)

where \( \mu_k \) is the chemical potential of the \( k \)th component, \( \mu_{k0} \) is its constant part, \( c_k \) is its concentration and \( \dot{N}_k \) is the reaction velocity.

(iv) Let us consider quasi-chemical processes

\[ \sum_i \nu_{is} A_{is} \rightleftharpoons \sum_j \nu_{js} A_{js}, \quad s = 1, 2, \cdots \]  

(5.5)

between the components. This describes a set of chemical reactions such as chain reaction, whose set is denoted by \( s \). It means that there are many chemical reactions that consist of a finite number set of molecules \( A_i \) and \( A_j \) labelled by \( i \) and \( j \).

(v) Let us denote by \( \dot{n}_s \) the reaction velocity of the process \( s \) from the left to the right. The reaction velocity \( \dot{N}_k \) can be written in the form:

\[ \dot{N}_i = -\sum_s \nu_{is} \dot{n}_s, \quad \dot{N}_j = \sum_s \nu_{js} \dot{n}_s. \]  

(5.6)

Through this linear transformation, the variables \( \dot{N}_i \) can be transformed to \( \dot{n}_s \). The number of new parameters \( \dot{n}_s \) may be less than \( \dot{N}_i \) and they may be independent variable.

(vi) Substituting Eq.(5.6) into Eq.(5.3), we find

\[ \dot{G} = \sum_s \left( \sum_j \nu_{js} \mu_j - \sum_i \nu_{is} \mu_i \right) \dot{n}_s = -\sum_s \Delta \mu_s \dot{n}_s \]  

(5.7)

where we have defined the affinity \( \Delta \mu_s \) of the reaction \( s \) as

\[ \Delta \mu_s \equiv \sum_k \nu_{ks} \mu_k = \sum_i \nu_{is} \mu_i - \sum_j \nu_{js} \mu_j. \]  

(5.8)

(vii) From the rate theory of chemical reaction, \( \dot{n}_s \) can usually be written in the form:

\[ J_s \equiv \dot{n}_s = \frac{1}{R_s} \left\{ e^{\frac{\sum_i \nu_{is} \mu_i}{kT}} - e^{\frac{\sum_j \nu_{js} \mu_j}{kT}} \right\}, \]  

(5.9)

where \( R_s \) is the chemical resistance of the process \( s \), which corresponds with the circumstance of the theory of rate process, and the quantity in the bracket
represents the $\mu$–field, that corresponds with the *circumstance of the theory of equilibrium*.

(viii) Inserting Eq.(5.9) into Eq.(5.7), we can see that $\dot{G}$ is equal to $kT\dot{H}$, where $H$ is the Boltzmann’s $H$–function. If the mean value of $H$ is taken in the momentum space and if it is assumed that $s$ represents only the rate determining precesses in the individual processes and that the higher term of $\dot{H}$ is negligible, then we obtain

$$\dot{G} = kT\dot{H}$$

$$= - \sum_s \frac{\nu_{ks}\mu_k}{R_s} \left\{ e^{\frac{\Sigma_i \nu_{is}\mu_i}{kT}} - e^{\frac{\Sigma_j \nu_{js}\mu_j}{kT}} \right\}$$

$$= - \sum_s \Delta \mu_s J_s = - T\dot{S}. \quad (5.10)$$

(ix) The reversal of the $\mu$–field can be interpreted if we consider the transition from the stage

$$\sum_i \nu_{is}\mu_i > \sum_j \nu_{js}\mu_j \rightarrow \sum_i \nu_{is}\mu_i < \sum_j \nu_{js}\mu_j. \quad (5.11)$$

In the above paper(1950,1951) Motoyosi Sugita was not able to present the detail of the proof of the conjecture. It was limited to suggest the existence. However, in the succeeding papers he argued the sketch of the conjecture and frequently tried to prove it.

5.2. Relationship between the Boltzmann’s $H$–function and the $\mu$–Field

5.3. Motoyosi Sugita’s Idea for the Proof of the Conjecture
6. The Ideas of Motoyosi Sugita as a Specific Development of Lars Onsager’s Lifework

In 1951 Motoyosi Sugita first presented the theory of the maximum principle in transient phenomena such as those discussed in the previous section (1951). This paper was entitled ”The Maximum Principle in the Transient Phenomena and the Application to Biology”, in Japanese. In this paper he first stated his vision and idea on the maximum principle in the transient phenomena. He argued the relationship between his idea of maximum principle and the existing old ideas such as the maximum-minimum principle in the Joule heat, the Boltzmann’s principle in the theory of gases, and the Onsager’s principle of the least dissipation of energy in the theory of irreversible processes (1931). He finally applied his idea to many biological systems such as the thermodynamics of metabolism, the relationship between the maximum principle and the metabolism, the origins of life, and the dynamic equilibrium, the relaxation oscillations, the wholeness of life, etc.

In the succeeding paper in 1952, he further studied the maximum principle in relation to the Boltzmann’s $H$–theorem (1952). This paper was entitled as ”The Relationship between the Boltzmann’s $H$–Theorem and the Dissipation Function”, in Japanese. This paper is a really instructive one. As is discussed in the previous section, his theory preceded the times of Prigogine (1971, 1999). So, in this section I would like to present his comparison between the Motoyosi Sugita’s theory and the Prigogine’s theory as well as Onsager’s theory (1931) and Katchalsky’s theory (1965, 1970, 1973). Fortunately for the Western people, these Japanese papers were summarized as the English versions (1953).

6.1. Relationship between the Boltzmann’s $H$–function and the Irreversible Work

As is shown in the previous section, we have obtained the Boltzmann’s $H$–function, especially for the case of chemical reactions. Motoyosi Sugita first applied his idea of the virtual heat that has been discussed in the section II to the irreversible work of the system.

In order to see the difference between the method of Motoyosi Sugita and that of Ilya Prigogine more easily, let us change the notation of Motoyosi Sugita to adjust with that of Prigogine. Let us denote by $i$ the internal system which is doing the irreversible work. Let us denote by $e$ the external
thermal reservoir, where we assume that no irreversible work has been done. By definition, we have
\[ G_i = U_i + PV_i - TS_i. \] (6.1)
If the process is the broad quasi-static change (under the isothermal and isopressure), then we have
\[ TdS_i = dU_i + PdV_i, \] (6.2)
which is equivalent to
\[ \dot{G}_i = 0. \] (6.3)
This is not satisfied when the irreversible work exists. In this case we have
\[ \dot{G}_i = \dot{U}_i + P\dot{V}_i - T\dot{S}_i, \] (6.4)
which is the isothermal irreversible work. Or equivalently,
\[ \dot{S}_i = \frac{\dot{U}_i + P\dot{V}_i}{T} - \frac{\dot{G}_i}{T}. \] (6.5)
On the other hand, since the heat \( \dot{U}_i + P\dot{V}_i \) comes out from the reservoir \( e \), we have for the reservoir \( e \)
\[ \dot{S}_e = -\frac{\dot{U}_i + P\dot{V}_i}{T}. \] (6.6)
Now we assume that there is no heat exchange otherwise, the total entropy of the system is given by
\[ \dot{S} = \dot{S}_i + \dot{S}_e = -\frac{\dot{G}_i}{T} > 0. \] (6.7)
Since there is no irreversible work in the reservoir \( e \), \( \dot{G}_e = 0 \). And since \( G \) is always decreasing, we can state that \( \dot{G}_i < 0 \). This \( \dot{G}_i \) is the irreversible work for the entire system and it is nothing more than "virtual heat" introduced by Motoyosi Sugita long ago. Then we have
\[ \dot{G}_i = -T\dot{S} = kTH. \] (6.8)
This suggests that there exists the maximum principle in the transient phenomena in terms of the Boltzmann’s \( H \)-function. Hence, his conjecture is
crucially important in the theory of non-equilibrium thermodynamics in the irreversible processes in the transient phenomena such as life. It also suggests the existence of the 4th law of thermodynamics.

6.2. Relationship between the Boltzmann’s $H$–function and the Dissipation Function

This argument can be generalized to the systems of flow dynamics or fluid dynamics. In this case there is matter exchange between the reservoir $e$ and the system $i$. Let us denote by $G_e$ the external part of $G$ and by $G_i$ the internal part of $G$, respectively. In the stationary state of the internal system $i$, the time derivative of $G_i$ vanishes (i.e., $\dot{G}_i = 0$). So, we have

$$\frac{dG}{dt} = \frac{d}{dt}(G_e + G_i) = \frac{dG_e}{dt} = [\dot{G}_i] < 0. \quad (6.13)$$

This $[\dot{G}_i]$ must have the same form as $kT\dot{H}$, which becomes the dissipation function of the system; that is $[\dot{G}_i] = -2\phi$. Hence, we must have

$$\frac{dG}{dt} = kT\dot{H} = -2\phi, \quad \text{or}, \quad (6.14)$$

or equivalently

$$\frac{dG}{dt} + 2\phi = 0. \quad (6.15)$$

This simple looking but very important relation was independently rediscovered by Katchalsky much later(1965,1970,1973). What is important here is that the above equation is valid even for open systems such as the flow or fluid dynamics as well as life systems.

Now Motoyosi Sugita imposes the maximum principle for this relation as follows: Suppose that $\frac{dG}{dt}$ (or $-2\phi$) represents the dissipation processes in the transient phenomena. For example, let us consider the metabolic system. Then, $\frac{dG}{dt}$ (or $-2\phi$) represents the reduction processes in the metabolic system. Then denote by $M$ the amount of creation per second, while denote by $|\frac{dG}{dt}|$ the dissipation per second. Let us define $M = |\frac{dG}{dt}|$. Then, we seek the extremum such that $|\frac{dG}{dt}|$ becomes the maximum under the restriction that $M = \text{const}$. This is the content of Motoyosi Sugita’s variation principle of the maximum in the transient phenomena(1952). Thus, I would like to summarize the Motoyosi Sugita’s maximum principle as follows:
Theorem 1 (Motoyosi Sugita’s Maximum Principle). Under the constraint $M = \text{const}$, find the maximum of the following equation:

$$M = \left| \frac{dG}{dt} \right|. \quad (6.16)$$

Thus Motoyosi Sugita challenged us who can prove this principle in general. Whoever can do so, then the 4th law of thermodynamics is proven.

6.3. Relationship between Motoyosi Sugita’s Theory and Lars Onsager’s Theory

Following the idea of Lars Onsager and Machlup (1931,1953,1953),

$$J_k = \frac{dx_i}{dt}, \quad X_j = \frac{\partial S_i}{\partial x_k}. \quad (6.17)$$

Here $J_k$ are called the ”generalized flows”, while $X_k$ are called the ”generalized forces”.

The famous linear relation is given by

$$X_i = \sum_j R_{ij} J_j, \quad (6.18)$$

where the coefficients $R_{ij}$ satisfy the reciprocal relation:

$$R_{ij} = R_{ji}. \quad (6.19)$$

This is the Onsager’s reciprocal theorem.

Solving Eq.(6.18) for $J_i$, we obtain

$$J_i = \sum_j L_{ij} X_j, \quad (6.20)$$

where $L_{ij} = R^{-1}_{ij} = L_{ji}$; the reciprocity holds true for $L_{ij}$.

This yields for the dissipation function:

$$\Phi(X_1, \ldots, X_n) = \frac{1}{2T} \sum_{i,j} L_{ij} X_i X_j = \frac{\phi(X)}{T}, \quad (6.21)$$

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where $\phi$ is the Rayleigh’s dissipation function.

Apart from the energy dissipation $\dot{S}^\ast(J_n)$ through the surface, we finally obtain

$$\dot{S}_i = 2\Phi(J_1, \cdots, J_n), \quad \dot{S}_i = 2\Phi(X_1, \cdots, X_n). \quad (6.22)$$

Since for the isothermal system the internal energy is kept constant, the rate of the Gibbs free energy $\dot{G}$ is related to the entropy change $\dot{S}_i$ such that $\dot{G} = -T\dot{S}_i$. Hence, we obtain

$$\dot{G} + 2\phi = 0, \quad (6.23)$$

where $\phi = T\Phi$.

Now I would like to note that the variational principle of the Onsager’s minimum or maximum principle falls into the Motoyosi Sugita’s maximum principle discussed before.

In the Onsager’s minimum or maximum principle, Onsager implicitly assumed that there exists a constant $M$ such that $M = |\dot{G}|$. Instead of showing that, Onsager also implicitly assumed that $X_k = \text{const.}$ for the variation or $J_k = \text{const.}$ for the variation, respectively.

Since the constraint either $X_k = \text{const.}$ or $J_k = \text{const.}$ is assumed, the extremum of either $J_k = \text{extremum}$ or $X_k = \text{extremum}$ after the variation is also constant. Hence, $M = |\dot{G}| = |2\phi|$ is constant as well. Thus, Onsager’s principle of the least dissipation of energy falls into the Motoyosi Sugita’s maximum principle as a special case.

Next let us consider the relationship between the Motoyosi Sugita’s $\mu$-field and the the above Onsager’s theory. As is shown in the above Onsager’s relation between the generalized forces and the generalized flows(or currents) are linear.

However, in the Motoyosi Sugita’s theory it is not so but it is nonlinear. Going back to Eq.(5.9), we hold the following relation:

$$\dot{S} = \sum_s \frac{\Delta \mu_s}{T} J_s = \sum_s \frac{\Delta \mu_s}{R_s T} \left\{ e^{\sum_i \nu_i \mu_i} - e^{\frac{\sum_i \nu_i \mu_i}{kT}} \right\}, \quad (6.24)$$

where from Eq.(5.31) or Eq.(6.17), $J_s$ is given by

$$J_s \equiv \frac{1}{R_s} \left\{ e^{\sum_i \nu_i \mu_i} - e^{\frac{\sum_i \nu_i \mu_i}{kT}} \right\}. \quad (6.25)$$

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6.4. Relationship between Motoyosi Sugita’s Theory and Ilya Prigogine’s Theory

Following the idea of De Donder(1936) and Prigogine(1971,1999), Prigogine assumes that the entropy increase of the system $\dot{S}_i$ is given by

$$\dot{S}_i = \sum_k \frac{A_k}{T} \xi_k \geq 0,$$

(6.26)

where Prigogine’s $A_k$ and $\xi_k$ are the affinity and the degree of the rate of the process of De Donder(1936) and they correspond to the Motoyosi Sugita’s $\Delta \mu_k$ and $\Delta n$, respectively.

The correspondence between the Motoyosi Sugita’s theory and the Ilya Prigogine’s theory is as follows:

<table>
<thead>
<tr>
<th>Sugita(1951)</th>
<th>Prigogine(1999)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta \mu_s = \sum_i \nu_i s \mu_i - \sum_j \nu_j s \mu_j$</td>
<td>$A_k = RT \ln \frac{R_{f_k}}{R_{b_k}}$</td>
</tr>
<tr>
<td>$J_s = \frac{1}{R_s} \left{ e^{\frac{s \nu_i s \mu_i}{R_s}} - e^{\frac{s \nu_j s \mu_j}{R_s}} \right}$</td>
<td>$v_k = R_{f_k} - R_{b_k}$</td>
</tr>
<tr>
<td>$\dot{S}_i = \sum_s \frac{\Delta \mu_s}{T} J_s$</td>
<td>$\dot{S}_i = \sum_k \frac{A_k}{T} v_k$</td>
</tr>
</tbody>
</table>

(6.27)
7. The Motoyosi Sugita’s Maximum Principle as the Pontryagin’s Maximum Principle

Now I would like to prove the conjecture of Motoyosi Sugita’s Maximum Principle, as the Pontryagin’s maximum principle in the modern optimal control theory.

7.1. Attractiveness of the Formulation of Classical Mechanics

What is most attractive in the theoretical framework of classical mechanics is as follows:

⋯⋯⋯ As if a pendulum moved automatically following the energy conservation law, the macroscopic biological system would move automatically following some unknown law of physics. If such a new type of law exists, it will be very nice. I would like to find such new principle of conservation law. This is our goal here.

7.2. Equations of Motion for the Open Dynamical System

\( x_i = \) the state variables (such as densities).
\( u_i = \) the control variables (could be any).
\( x = (x_1, \ldots, x_n) \).
\( u = (u_1, \ldots, u_r) \).

The equation of motion for the dynamical system:

\[
\begin{align*}
\dot{x}_1 &= f_1(x_1, \ldots, x_n, u_1, \ldots, u_r, t) \\
\dot{x}_2 &= f_2(x_1, \ldots, x_n, u_1, \ldots, u_r, t) \\
&\vdots \\
\dot{x}_n &= f_n(x_1, \ldots, x_n, u_1, \ldots, u_r, t)
\end{align*}
\] (7.1)

Simply,

\[
\frac{dx_i}{dt} = \dot{x}_i = f_i(x, u, t), \quad (i = 1, \ldots, n)
\] (7.2)
As in the case of classical mechanics, once we regard the state variables \( x \) as the classical variables, we can define a Hamiltonian.

Let us denote by \( \psi = (\psi_1, \ldots, \psi_n) \) the adjoint vector for the adjoint variables \( \psi_i \).

Let us define the Hamiltonian:

\[
H_0 = \sum_{i=1}^{n} \psi_i \dot{x}_i = \sum_{i=1}^{n} \psi_i f_i(x, u, t),
\]

(7.3)

According to the Pontryagin’s theory of the optimal control, we can prove the Hamilton equation:

\[
\frac{dx_i}{dt} = \frac{\partial H_0}{\partial \psi_i}, \quad \frac{d\psi_i}{dt} = -\frac{\partial H_0}{\partial x_i}.
\]

(7.4)

The standard Hamiltonian in physics has units of energy [Joules], on the other hand, the Pontryagin’s Hamiltonian in the Optimal control theory could be any. For our case it has units of work rate, \( \mathcal{W} = \frac{dE}{dt} \) [Joules/sec], or power, \( \mathcal{P} \), [Watts].

As we have discussed before, the rate of Gibbs free energy:

\[
\dot{G} = \sum_k \mu_k \dot{N}_k.
\]

(7.5)

looks much like the above Hamiltonian \( H_0 \).

To understand this point, if \( f_i(x, u, t) \) does not depend upon \( x_i \) such as \( f_i(x, u, t) = f_i(u, t) \), then Eq.(7.4) provides

\[
\frac{d\psi_i}{dt} = 0, \quad \psi_i = \text{const.} \equiv \mu_i.
\]

(7.6)

Substituting this in the above original Pontryaginian of \( H_0 \), we obtain

\[
H_0 = \sum_{i=1}^{n} \mu_i \dot{x}_i = \sum_{i=1}^{n} \mu_i f_i(u, t).
\]

(7.7)

This is nothing but the standard time-derivative of Gibbs free energy:

\[
G = \sum_j \mu_j N_j, \quad x \equiv (N_1, \ldots, N_n) \quad \mu \equiv (\mu_1, \ldots, \mu_n), \quad \text{we obtain}
\]

\[
\frac{dG}{dt} = \sum_j \mu_j \frac{dN_j}{dt} = \sum_{i=1}^{n} \mu_i \dot{x}_i = H_0.
\]

(7.8)

This expression means that
the rate of Gibbs free energy is conserved under the time-development of the system.

This supports the first part of the conjecture for the maximum principle of Motoyosi Sugita, where he assumed that \( M = \text{constant} \) for \( M = \frac{dG}{dt} \).

Thus, I would like to first claim that

\[ M \text{ should be the absolute value of the Hamiltonian } \mathcal{H}_0 \text{ in the sense of Pontryagin.} \]

### 7.3. Proof of the New Conservation Law

The general proof of the conservation of the Pontryagin’s Hamiltonian is quite complex. It is not so convenient to describe the detail in short here. Since the proof is given in the textbook of Pontryagin et. al., we skip the detail. Therefore, I would like to describe the essence of the proof.

As before, we start with the dynamics given by Eq.(1.1) or Eq.(7.2).

Let us find the equilibrium state taking the variation \( \delta x_i \) such as

\[
y_i(t) = x_i(t) + \varepsilon \delta x_i(t), \quad (i = 1, \ldots, n), \tag{7.9}
\]

where \( \varepsilon \) is a small positive value and we assume that the initial condition for \( \delta x_i \) such that it starts with the value:

\[
\delta x_i(t_0) = \xi_{i0}. \tag{7.10}
\]

Substituting the above into Eq.(7.1), expanding it with respect to \( \varepsilon \), we can obtain the linearized equations of motion:

\[
\frac{d(\delta x_i)}{dt} = \sum_{j=1}^{n} \frac{\partial f_i(x(t), u(t))}{\partial x_j} \delta x_j \equiv \sum_{j=1}^{n} J_{ij} \delta x_j. \tag{7.11}
\]

where the matrix \( \hat{J} \equiv (J_{ij}) \) is called the Jacobian or Jacobi matrix.

If we consider the stability of the system, then we would like to find the eigenvalues of the above equation around the stationary point as follows:

\[
\begin{align*}
0 &= f_1(x_1, \ldots, x_n, u_1, \ldots, u_r, t) \\
0 &= f_2(x_1, \ldots, x_n, u_1, \ldots, u_r, t) \\
& \vdots \\
0 &= f_n(x_1, \ldots, x_n, u_1, \ldots, u_r, t)
\end{align*}
\tag{7.12}
\]
Solving Eq.(7.12) for $x_i$ ($i = 1, \ldots, n$) under fixing as $u_k \equiv \tilde{u}_k$, where $\tilde{u}_k$ ($k = 1, \ldots, r$) are constants, we obtain the dynamically equilibrium states or the stationary states:

$$x_i = \bar{x}_i. \tag{7.13}$$

Similar to Eq.(7.9), we expand the state vector as

$$x_i(t) = \bar{x}_i + \varepsilon \delta x_i(t). \tag{7.14}$$

Substituting this into Eq.(7.2), we similarly obtain

$$\frac{d(\delta x_i)}{dt} = \sum_{j=1}^{n} \frac{\partial f_i(\bar{x}, \tilde{u})}{\partial x_j} \delta x_j \equiv \sum_{j=1}^{n} \tilde{J}_{ij} \delta x_j. \tag{7.15}$$

For the special values of $\tilde{u}$, we define

$$\delta x_i(t) = (\delta x_i)_{in} e^{\omega t}, \quad (i = 1, \ldots, n). \tag{7.16}$$

Then substituting the above into Eq.(7.15), we obtain

$$\omega (\delta x_i)_{in} = \sum_{j=1}^{n} \tilde{J}_{ij} (\delta x_j)_{in}. \tag{7.17}$$

This yields the characteristic equation:

$$\det |\omega \delta_{ij} - \tilde{J}_{ij}| = 0. \tag{7.18}$$

By investigating the characteristics of $\omega$, we can find the stability condition of the equilibrium state such that if all real parts of the eigenvalues are negative, then the system is stable. This is the linear stability analysis mentioned by Prigogine(1971,1999).

In the modern optimal control theory, we do not do that. Instead of doing so, we define the adjoint matrix, $\tilde{J}$:

$$\tilde{J}_{ij} \equiv - \frac{\partial f_j(x(t), u(t))}{\partial x_i} = -J_{ji}. \tag{7.19}$$

Define the following dynamical equations for the new functions, $\psi_i$:

$$\frac{d\psi_i}{dt} = - \sum_{j=1}^{n} \frac{\partial f_j(x(t), u(t))}{\partial x_i} \psi_j = \sum_{j=1}^{n} \tilde{J}_{ij} \psi_j, \tag{7.20}$$

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where \( \tilde{J} = - \hat{J}^t \), \( t \) meaning transpose of \( \hat{J} \).

We then define the Pontryagin’s Hamiltonian as

\[
\mathcal{H}_0 = \sum_{i=1}^{n} \psi_if_i(x,u).
\] (7.21)

Let us prove that \( \mathcal{H} \) is a constant of motion in the nonlinear dynamical systems for the state variables.

Differentiating with respect to time, we have

\[
\frac{d\mathcal{H}_0}{dt} = \sum_{i=1}^{n} \left\{ \frac{d\psi_i}{dt} f_i(x,u) + \psi_i \frac{df_i(x,u)}{dt} \right\}.
\] (7.22)

And we have

\[
\frac{df_i(x,u)}{dt} = \sum_{j=1}^{n} \frac{\partial f_i(x,u)}{\partial x_j} \dot{x}_j + \sum_{k=1}^{r} \frac{\partial f_i(x,u)}{\partial u_k} \dot{u}_k,
\] (7.23)

for \( i = 1, \ldots, n \).

Substituting this into Eq.(7.22), we obtain

\[
\frac{d\mathcal{H}_0}{dt} = \sum_{i=1}^{n} \frac{d\psi_i}{dt} f_i(x,u) + \sum_{i=1}^{n} \sum_{j=1}^{n} \psi_i \frac{\partial f_i(x,u)}{\partial x_j} \dot{x}_j
\]

\[
= \sum_{i=1}^{n} \frac{d\psi_i}{dt} f_i(x,u) + \sum_{i=1}^{n} \sum_{j=1}^{n} \psi_i J_{ij} \dot{x}_j
\]

\[
= \sum_{i=1}^{n} \frac{d\psi_i}{dt} f_i(x,u) + \sum_{i=1}^{n} \sum_{j=1}^{n} \psi_i J_{iy} f_j(x,u)
\]

\[
= \sum_{i=1}^{n} \sum_{j=1}^{n} \left( \frac{d\psi_j}{dt} \delta_{ij} + \psi_i J_{ij} \right) f_j(x,u).
\] (7.24)

Here we have assumed that the extremum condition for \( f_i(x,u) \) with respect to \( u_j \) such that

\[
\frac{\partial f_i(x,u)}{\partial u_j} = 0, \quad (j = 1, \ldots, r).
\] (7.25)
By definition, this is equivalent to the following optimal condition:

\[ \frac{\partial \mathcal{H}_0}{\partial u_j} = 0, \quad (j = 1, \ldots, r), \]  

(7.26)

where the maximum condition is also given by

\[ \sum_{i,j} \xi_i \left( \frac{\partial^2 \mathcal{H}_0}{\partial u_i \partial u_j} \right) \xi_j \leq 0, \quad (i, j = 1, \ldots, r). \]  

(7.27)

If the condition is for the minimum then the inequality has to be reversed.

Let us now impose

\[ \frac{d\psi_i}{dt} + \sum_{j=1}^n \psi_j J_{ji} = 0, \]  

(7.28)

equivalently,

\[ \frac{d\psi_i}{dt} = -\sum_{j=1}^n J_{ji} \psi_j = \sum_{j=1}^n \bar{J}_{ij} \psi_j \]  

(7.29)

This equation is called the adjoint equation for Eq. (7.11).

The new set of variables \( \psi = (\psi_1, \ldots, \psi_n) \) play the role of the dynamical chemical potentials of the system, which depend upon time such that the values are dynamically changing according to the control variables \( u(t) = (u_1(t), \ldots, u_m(t)) \).

Substituting Eq. (7.28) into Eq. (7.24), we finally obtain

\[ \frac{d\mathcal{H}_0}{dt} = 0. \]  

(7.30)

This means that \( \mathcal{H}_0 \) is a constant of motion. Namely,

\[ \mathcal{H}_0 = \mathcal{M} = \text{const.} \]  

(7.31)

Hence, we have proven that the Pontryagin’s Hamiltonian (the Pontryaginian) is conserved in the course of time-development. Thus, the proof is obtained.
7.4. Generalization of the Pontryagin’s Hamiltonian to the System with a Constraint

Define a quantity:
\[
\mathcal{J} = \int_{t_0}^{t_1} f_0(x(t), u(t), t) \, dt.
\] (7.32)

This is called the performance index or the cost function or the effectiveness.

This quantity takes the minimum value or maximum value in the course of the time-development of the system in between \(t_0\) and \(t_1\).

\[ \delta \mathcal{J} = 0. \] (7.33)

In this more general case than the previous one, we can define Pontryagin’s Hamiltonian \(\mathcal{H}_1\) as

\[
\mathcal{H}_1 \equiv \mathcal{H}_0 - f_0(x(t), u(t), t)
= \sum_{i=1}^{n} \psi_i(t) \dot{x}_i(t) - f_0(x(t), u(t), t)
= \sum_{j=1}^{n} \psi_j f_i(x(t), u(t), t) - f_0(x(t), u(t), t).
\] (7.34)

Obviously this has the form of the Hamiltonian in classical mechanics such as

\[ H = \vec{p} \cdot \dot{x} - L. \]

Do not confuse this \(\mathcal{H}_1\) of Eq.(7.34) with \(\mathcal{H}_0\) of Eq.(7.21). Because the constraint of Eq.(8.32) is included in the Pontryagin’s Hamiltonian \(\mathcal{H}_1\) in this case, while no constraint is included in the previous Hamiltonian \(\mathcal{H}_0\). Therefore, I put 0 and 1 to escape from confusion.

Thus, in the previous Hamiltonian the maximum can take nonzero value for \(M\), but in the above Hamiltonian, the maximum has to be always zero [see below].

Let us now suppose the following new variable \(x_0(t)\) by

\[ x_0(t) = \int_{t_0}^{t} f_0(x(t), u(t), t) \, dt. \] (7.35)
By differentiation we find
\[ \frac{dx_0(t)}{dt} = f_0(x(t), u(t), t). \] (7.36)

Let us define a fictitious parameter
\[ \psi_0 = -1. \] (7.37)

Then we can represent the above Eq.(7.34) more compactly such as
\[ H_1 = \sum_{j=0}^{n} \psi_j f_j(x, u, t). \] (7.38)

However, at this time the system must obey the following nonlinear dynamics:
\[ \dot{x}_i = f_i(x, u, t), \quad (i = 0, 1, \ldots, n) \] (7.39)

As before, we then have the equations of motion similar to Eq.(7.4) and Eq.(7.5):
\[ \begin{align*}
\frac{dx_i}{dt} &= \frac{\partial H_1}{\partial \psi_i}, \\
\frac{d\psi_i}{dt} &= -\frac{\partial H_1}{\partial x_i},
\end{align*} \] (7.40)

where \( x(t) \equiv (x_0(t), x_1(t), \ldots, x_n(t)). \)

Here we would like to note that the first equation of Eq.(7.40) for \( \psi_0 \) reduces to \( \dot{\psi}_0 = 0 \), since \( f_0(\vec{x}, \vec{u}, t) \) does not depend upon \( x_0 \) at all. We also have the following constraints as before:
\[ \frac{\partial H_1}{\partial u_j} = 0, \quad (j = 1, \ldots, r), \] (7.41)

where the maximum condition is also given by
\[ \sum_{i,j} \xi_i \left( \frac{\partial^2 H_1}{\partial u_i \partial u_j} \right) \xi_j \leq 0, \quad (i, j = 1, \ldots, r). \] (7.42)

If we take \( \psi_0 = 1 \), then the above condition for the maximum principle turns out to be the one for the minimum principle.

Now we can summarize the very important theorem which is known as the **Pontryagin’s maximum principle** in the optimal control theory. This theorem is described as follows:
Theorem 2 (Pontryagin’s Maximum Principle). At some control vector value \( u(t) = u \),
\[
H_1(\psi(t), x(t), u(t), t) = 0. \tag{P}
\]

7.5. The 4th Law of Thermodynamics

Now, let us go back to the maximum principle of Motoyosi Sugita. We can restate it as follows:

Theorem 3 (Modern Version of the Motoyosi Sugita’s Maximum Principle). Suppose that the rate of the Gibbs free energy \( \frac{dG}{dt} \) is given as the Pontryagin’s Hamiltonian \( H_0 \) as before. Let us define the Pontryagin’s Hamiltonian with a constraint such that
\[
H_1 = \sum_{j=0}^{n} \psi_j f_j(x, u, t), \tag{7.44}
\]
where the state variables are assumed to obey the following dynamical equations:
\[
\dot{x}_i = f_i(x, u, t), \quad (i = 0, 1, \ldots, n). \tag{7.45}
\]
Then, if the system advances under the optimal control of the control variables \( u \), then there exists a maximum of the Hamiltonian \( H_1 \) such that
\[
|H_1|_{max} = 0. \tag{7.46}
\]
And in this moment, always the following equations hold: The equations of motion:
\[
\frac{dx_i}{dt} = \frac{\partial H_1}{\partial \psi_i}, \quad \frac{d\psi_i}{dt} = -\frac{\partial H_1}{\partial x_i}, \tag{7.47}
\]
for \( i = 1, \ldots, n \), the optimality condition:
\[
\frac{\partial H_1}{\partial u_s} = 0, \quad s = 1, \ldots, r, \tag{7.48}
\]
and the maximum condition:
\[
\sum_{s,t} \xi_s \left( \frac{\partial^2 H_1}{\partial u_s \partial u_t} \right) \xi_t \leq 0, \quad s, t = 1, \ldots, r. \tag{7.49}
\]
Here in Eq.(7.49) if $\psi_0 = 1$ then we change the inequality to $\geq 0$ such that the maximum condition becomes the minimum condition.

I believe that this principle is exactly nothing more than the 4th law of thermodynamics in terms of the language of the modern control theory.

The above approach of Pontryagin’s maximum principle is very general and therefore it should not be restricted within thermodynamics. However, I would like to see the relationship between the Motoyosi Sugita’s maximum principle and the Pontryagin’s maximum principle.

Let us apply the above method to thermodynamics especially for the isothermal system where $T = \text{const.}$

In order to do it, let us consider the Onsager’s theory. We must assume that the dissipated energy from the system is becoming the virtual heat such that

$$
\dot{S} = 2\Phi,
$$

where $\Phi$ is the dissipation function of Rayleigh such that

$$
\Phi = \frac{1}{2} \sum_{i,j} R_{ij} J_i J_j
$$

and

$$
\dot{S} = \sum_i X_i J_i.
$$

This restriction imposes the Onsager’s variation principle:

$$
\Phi(x(t), u(t), t) - \dot{S}(x(t), u(t), t) = \text{minimum},
$$

or equivalently

$$
\delta[\Phi(x(t), u(t), t) - \dot{S}(x(t), u(t), t)] = 0.
$$

This provides $X_i = \sum_j R_{ij} J_j$.

This is the heart of the Onsager’s principle of the least dissipation of energy. It plays the role of Lagrangian in classical mechanics. Because when we impose that the action of energy change from the dissipation energy to the virtual heat is as fast as possible, then we take variation for it.

Therefore, once we regard this variational constraint as $f_0$ in Eq.(7.44), then we obtain the Pontryagin’s Hamiltonian for isothermal system as

$$
\mathcal{H}_1 = \sum_{j=1}^{n} \psi_j f_j(x, u, t) + \psi_0 f_0(x, u, t)
$$

$$
= \sum_{j=1}^{n} \psi_j f_j(x, u, t) - T[\Phi(x, u, t) - \dot{S}(x, u, t)]
$$

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\[ \frac{dG}{dt} + T \left[ \dot{S}(x, u, t) - \Phi(x, u, t) \right] \] (7.53)

where we have taken as \( \psi_0 = -T \).

If we adjust with the definition of Gibbs free energy, then we must regard the Hamiltonian \( \mathcal{H}_1 \) in the left hand as the power \( \mathcal{P} = \frac{dE}{dt} \). This yields

\[ \mathcal{P} = \frac{dE}{dt} = \mathcal{H}_1. \] (7.54)

This Hamiltonian was first found by the author two years ago (Iguchi, 2014).

Thus, as long as we take the extremum using Eq. (7.46), we have to obtain the following simple relation

\[ \frac{dG}{dt} = \sum_{j=1}^{n} \psi_j f_j(x, u, t) = -T \left[ \dot{S}(x, u, t) - \Phi(x, u, t) \right]. \] (7.55)

This is the most general expression for the Gibbs equation generalized from the standard one in the textbook of thermodynamics:

\[ \frac{dG}{dt} = \sum_{i=1}^{n} \mu_i \dot{N}_j = -T \left[ \dot{S}(x, u, t) - \Phi(x, u, t) \right]. \] (7.56)

Furthermore, if we impose the \textit{quadratic relation} for the dissipation function of \( \dot{S} = 2\Phi \) [Eq. (7.50)], then we substitute it into the above. We finally obtain the following relation:

\[ \frac{dG}{dt} = \sum_{i=1}^{n} \mu_i \dot{N}_j = -T \Phi(x, u, t) = -\phi. \] (7.57)

Namely,

\[ \frac{dG}{dt} + \phi = 0. \] (7.58)

Hence,

\[ \frac{dG}{dt} = -\phi \leq 0. \] (7.59)

Obviously, in the above equation the factor is different from the one before such as in Eq. (6.15). This depends upon the choice for the function \( f_0 \).
If we choose another form for the constraint such as
\[ \dot{S} = \text{minimum}, \quad \text{or} \quad \delta[\dot{S}] = 0 \quad (7.60) \]
which means the least production of entropy, then we have to set
\[
\mathcal{H}_1 = \sum_{j=1}^{n} \psi_j f_j(x, u, t) + \psi_0 f_0(x, u, t)
\]
\[
= \sum_{j=1}^{n} \psi_j f_j(x, u, t) + T\dot{S}(x, u, t)
\]
\[
= \frac{dG}{dt} + T\dot{S}(x, u, t). \quad (7.61)
\]
From the theorem, we find
\[
\frac{dG}{dt} + T\dot{S}(x, u, t) = 0. \quad (7.62)
\]
Hence, we obtain
\[
\frac{dG}{dt} + T\dot{S}(x, u, t) = \frac{dG}{dt} + 2\phi = 0. \quad (7.63)
\]
This coincides with the previous result such as Eq.(6.15).
8. Summary

(i) The personal history of Motoyosi Sugita:
his birth,
education,
working,
marriage,
visits,
publications,
his research history, etc.

(ii) His bright ideas:
the concept of broad quasi-static change,
the concept of virtual heat,
the concept of irreversible cycle.

(iii) The diffusion phenomena:
the Langevin equation,
the mixing entropy and free energy,
the number of partition.

(iv) The concepts in thermodynamics of transient phenomena:
the field of chemical potential,
the relationship between cooperative phenomena and the chemical potential,
etc.

(v) \( |\dot{G}| = \max \) conjecture:
the existence of the 4th law of thermodynamics,
the relationship between the Boltzmann’s \( H \)-theorem and the \( \mu \)-field (i.e.,
the field of chemical potential).

(vi) The relationship between the Motoyosi Sugita’s theory and the Onsager–Prigogine theory.

(vii) The maximum principle in the modern optimal control theory:

The Pontryagin’s maximum principle can be regard as a key to prove the existence of the 4th law of thermodynamics, when it is applied to non-equilibrium thermodynamics in the transient phenomena.
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