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Thermomechanical Dynamics (TMD) Applied to the Physical Concepts of the Zeroth Law and the Third Law of Thermodynamics

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Abstract

The zeroth law of thermodynamics, the Nernst-Simon and Planck statements of the third law of thermodynamics and the unattainability statement of the absolute temperature, $T = 0$, are discussed by thermomechanical dynamics (TMD) which is a classical theory of thermodynamics extended to study thermal transitions from thermodynamic equilibrium to nonequilibrium irreversible states (NISs). The method of TMD has been successfully applied to mechanisms of heat engines (a drinking bird, a low temperature Stirling engine and thermoelectric energy conversion technologies). The TMD is applied to the thermal phase transitions from thermodynamic equilibrium to NISs, and dissipative equations of motion for phase transition mechanism of heat engines in general are studied. The results are thermodynamically consistent and have produced new technical applications on a thermoelectric power-conversion method and devices for sustainable environmental goals. The method of TMD is applied to understand consistent thermodynamic concepts of the zeroth and the third law of thermodynamics and the unattainability statement, $T = 0$. The analyses help extend thermodynamics to NISs.

Keywords

The Nernst-Simon and Planck Statements of the Third Law of Thermodynamics, The Unattainability Statement of the Absolute Temperature $T = 0$, The Zeroth Law of Thermodynamics, Thermodynamic Measurement and Quantum Measurement, The Thermodynamic Internal Time *vs.* the External Time

1. Introduction: The Revolution of Thermodynamics

Thermodynamics is the study of heat and work to produce *thermomechanical* motion, and it has contributed to construct improved and refined heat engines since the industrial revolution from 18th century, such as steam locomotives, automobiles and refrigerators. Moreover, it has evolved to jet engines, as well as thermal and nuclear power stations with advanced technologies and available newly discovered energy resources. Accordingly, thermodynamics has evolved from equilibrium thermodynamics to the theory of nonequilibrium and irreversible processes [1]-[3]. The content of modern thermodynamics has radically progressed from hadron, chemical, molecular interactions to biological systems, electromagnetic radiation, heat engines and astrophysical problems [4]-[6], and to the larger subject of work and energy exchanges among dynamical systems of dissipative structure [7] [8].

Classical and quantum statistical mechanics are employed to explain thermodynamic phenomena of large systems from microscopic quantum to macroscopic thermodynamic systems, and properties of thermodynamic equilibrium states are established among average values and thermal fluctuations characterized by a probability distribution function. The governing distribution function is constructed by a complex, classical or quantum many-body Lagrangian or Hamiltonian. Although the central quest of statistical approaches is to understand macroscopic phenomena, the method is liable to restrict thermodynamics to near equilibrium, or to infinitely slow reversible processes, or systems of infinite time, particles and resources (heat baths), for mathematical strictness. It is fundamental to perceive that thermodynamic equilibrium designates a state of complete balance defined precisely by all macroscopic heat and energy, matter and particles.

The macroscopic world is composed not only of delicate and stable interactions of thermodynamic states, but also of enormous and extreme states of exploding and flowing of heat, energy, matter and particles. The fluxes of heat, energy, matter and particles are building blocks of fundamental structures from microscopic properties of matter, cells and organisms to macroscopic dynamic nature and universe. The macroscopic world in which we live is mechanical and thermodynamic in nature. Though the electromagnetic and quantum phenomena emerge from microscopic scales, quantitative measurement and descriptions of extreme heat and energy are confined in macroscopic physical quantities, such as internal energy, work, heat, entropy, temperature and other thermodynamic potential functions. Hence, the measurable thermodynamic physical quantities comply with *extremum principles* as well as the conservation laws of thermodynamics; in other words, the evolution to thermodynamic equilibrium corresponds to extremum of a thermodynamic quantity under relevant thermodynamic conditions.

Thermodynamic principle is fundamental for the analysis of macroscopic world; however, interactions of thermodynamic states are so complicated that the analysis is usually restricted in processes that have initial and final thermodynamic states and near equilibrium states. It is recognized that almost all systems in nature are not in thermodynamic equilibrium, and they are changing continuously or discontinuously over time by exchanging fluxes of heat, energy, matter and particles. Therefore, nonequilibrium thermodynamics has been proposed to study time-dependent progresses of state functions internally connected to those of thermal equilibrium states. The time-dependent thermodynamic states are essentially in nonequilibrium states.

In a thermal process, it is said *reversible*, when changes of systems and the environment are reversed to their initial states with time-symmetric procedure, but if it is not possible to reverse or restore time-symmetric procedure to their initial states, the process is called *irreversible*, which results in entropy productions. The nonequilibrium thermodynamic states generally induce irreversible states, resulting in nonequilibrium irreversible states (NISs). This is the macroscopic world of thermodynamics that *entropy productions*, *time-symmetry breaking* and *causality* exist. The entropy-increasing irreversible processes are abundant in nature and modern technologies, such as energy flows in turbines and jet engines, ignitions and detonations [9] [10], solar and wind energy-conversion technologies [11], electromagnetic radiations and interactions, astronomical high density matter, chemical reactions and self-organization, dissipative structures in cells and living beings [12]-[14].

All of the research topics in NISs seems to be too advanced for beginners, however, it is fortunate that there are excellent, simple and amusing experimental devices for people in general to study and explicitly observe thermomechanical motion in NISs. They are well-known experimental devices of heat engines: a drinking bird and a low temperature Stirling engine, shown in **Figure 1** and **Figure 2**. We proposed a theoretical model for NISs, *thermomechanical dynamics* (TMD) to study thermomechanical state of a drinking bird, a low temperature Stirling engine. In addition, the TMD can be extended to heat engines in general.

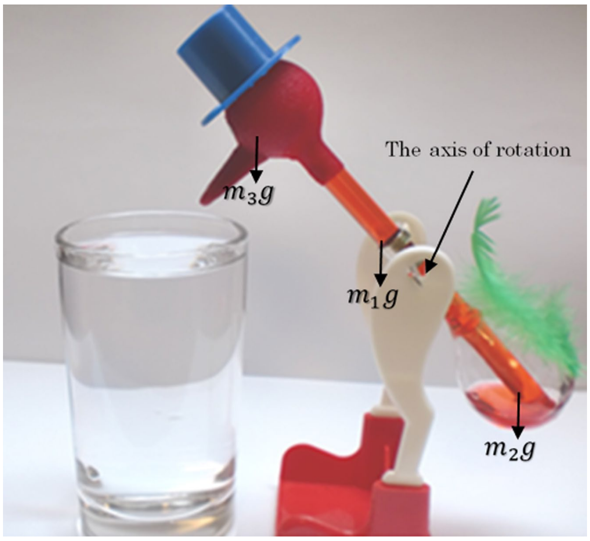

Figure 1. A drinking bird's motion is performed in nonequilibrium irreversible states (NISs) [17].

Figure 2. A low temperature Stirling engine (LTSE) works with heat flows (entropy flows) in NISs [18].

The method of TMD is a classical approach proposed by the authors, along the work of Gibbs' thermodynamics. Based on the fundamental thermodynamic concept, the theory of TMD is consistently applied to nonequilibrium irreversible states (NISs) of heat engines and phase transition phenomena. The thermomechanical motion of heat engines is self-consistently solved with the method of TMD. This is essential to realize that heat engines in general are examples of the transition from thermodynamic equilibrium to a nonequilibrium irreversible state and vice versa. Therefore, heat engines seem to be reasonable experimental devices to study thermomechanical motion. The concept of heat engines is extremely useful and fundamental for nonequilibrium thermodynamics and phase transitions among thermodynamic equilibrium and NISs. Readers who are interested in theoretical structure and discussions should be directed to references [15]-[18], and the method of TMD is explained in sec. 3, in order to make discussions self-contained.

The nonequilibrium irreversible motion of a drinking bird and a low temperature Stirling engine were self-consistently solved by the method of TMD [17] [18]. The self-consistent TMD analyses have shown remarkable results on phase transitions from thermal equilibrium to NISs, and time-dependent phase-transition solutions are discovered and expressed by nonlinear differential equations with time-dependent coefficients (NDE-TC). Starting with an initial thermal equilibrium, a thermodynamic system proceeds to NISs and evolves to a thermal state which is denoted as a *metastable state* determined by extremum of a *thermodynamic function*. Equations of motion for a physical system are usually nonlinear differential equations with constant coefficients (NDE-CC), and a nonlinear differential equation with constant coefficients have bifurcation solutions, which were first reported and discussed by Henri Poincaré in 1885 [19], and bifurcation phenomena have been studied by many researchers in the field of mathematics, physics, biophysics and so forth.

This is important to know that solutions of NDE-TC produce independent solutions corresponding to NISs, whereas a NDE-CC yields solutions corresponding to thermodynamic equilibrium. The drinking bird equation of motion, Starling engines and heat engines in general are excellent experimental machines to show phase transitions from thermal equilibrium to NISs. The time-dependent coefficients are the fundamental key to a drinking bird's water-drinking motion, heat engines and phase transitions to NISs. A phase transition mechanism can be expressed by nonlinear differential equations with time-dependent coefficients (NDE-TC). The time-asymmetry appears in NISs, resulting in a *dissipative structure* associated with energy and entropy flows, producing direction of time and retardation effects [20]-[23].

Since the NDE-TC has a complete solution evolving from a simple swinging motion to an exact water-drinking motion, the solution is termed as *bifurcation-integration* solution [24]. Researchers in mathematics, physics and sciences in general should investigate the fundamental properties of bifurcation-integration solutions. The nonlinear differential equations with time-dependent coefficients could have far more fundamental physical meanings contributing to sciences. The bifurcation-integration solutions and TMD method produced self-consistent, time-dependent dynamical quantities progressing to a metastable state, such as internal energy $\mathcal{E}(t)$, thermal work $W(t)$, entropy $\mathcal{S}(t)$ and nonequilibrium temperature $\tilde{T}(t)$.

The responses of heat engines to external heat flows are clearly examined by time-dependent thermodynamic quantities ($\mathcal{E}(t)$, $W_{th}(t)$, $\mathcal{S}(t)$, $\tilde{T}(t)$) in NISs and analyzed numerically. The nonequilibrium temperature, $\tilde{T}(t)$, has shown physical properties consistent with empirical results of heat engines, and it is very useful to study stability and changes of thermal states, ignition and detonation, frictional heat dissipations and diffusion mechanism. The results elucidated a new physical property of temperature. The temperature, $\tilde{T}(t)$, is a dynamical quantity of thermal system, which signifies how slowly or violently, an internal thermal state responses against external disturbances and heat flows.

The method of thermomechanical dynamics (TMD) has been applied to thermal motion of heat engines; empirical results and properties of heat engines are reasonably examined and reproduced. The physical and mathematical analyses of phase transitions from thermodynamic equilibrium to NISs in heat engines are self-consistently resolved and expressed by nonlinear differential equations with time-dependent coefficients (NDE-TC) [24]. The TMD analyses have also contributed to generate an important technology for thermoelectric energy conversions, applicable for environmental clean energy technologies [25]-[27]. The method of TMD is thermodynamically consistent, therefore, we apply the method of TMD to laws of thermodynamics, such as the zeroth law of thermodyanamics; the Nernst-Simon and Planck statements of the third law of thermodynamics; the unattainability statement of the absolute temperature, $T = 0$. The application yields new interpretations and profound understandings, which is the purpose of the current paper.

The Nernst-Simon and Planck statements of the third law of thermodynamics and the unattainability, $T=0$ with entropy $S(T)\to 0$, are discussed in detail in sec. 2. The physical interpretation of the Zeroth law of thermodynamics is discussed in sec. 2.1, which reveals and emphasizes that the zeroth law of thermodynamics is for understanding the concept of entropy, not for temperature. Classical and quantum statistics, probabilistic approaches for cooling a system are discussed in sec. 2.2, and the analyses of the unattainability $T_0=0$ follows in sec. 2.3. The method of thermomechanical dynamics (TMD) for nonequilibrium irreversible states is reviewed in sec. 3, and the heat-picture, $Q(t)$-picture in the TMD approach is briefly explained in 3.1. The consequences of the TMD analysis on the third law of thermodynamics are discussed in sec. 4. The arrow of time, thermodynamic measurement and quantum measurement are discussed in sec. 5, and conclusions and perspectives are in sec. 6.

2. The Nernst-Simon and Planck Statements of the Third Law of Thermodynamics and the Unattainability $T=0$

We briefly summarize the physical meaning of the nonequivalence of the Nernst-Simon, Plank statements and unattainability statements of the third law of thermodynamics, discussed by J. C. Wheeler [28] [29], to examine the physical meanings of the third law of thermodynamics and the unattainability $T=0$.

The Nernst-Simon and Planck version of the third law of thermodynamics is often expressed as:

$$\lim_{T\to 0} S(T,V,N)=0, \tag{1}$$

where T, V and N are respectively the absolute temperature, volume and number of particles. Although the statement (1) seems obvious for defining the property of entropy at absolute zero, the expression (1) is soon understood physically inappropriate because $T=0$ is difficult to attain technically and physically. The following physical argument is specifically pointed out; the variation of a finite absolute temperature $T\to 0$ in a thermal system with $S=0$ is not possible, because it is incapable of transferring heat to any other system, no matter how low its temperature can be. In other words, in a system with $S=0$ state, one cannot change $T\to 0$ by way of any physical process; a substance with zero entropy cannot give up heat to any reservoir of a finite temperature [28] [29]. In a thermal equilibrium at a positive temperature, the variation of T is only induced by the variation of entropy, $\Delta S=S(T,V,N)-S_0$ (S_0 is the entropy at a reference equilibrium state), meaning that the existence of ΔS or heat ΔQ is fundamental than the variation of T. The absolute temperature T is changed only if $\Delta S\neq 0$; the thermodynamic principle must be strictly maintained. Therefore, the statement (1) must be restated in order to avoid confusions.

A stable thermal system is expressed as a *metastable equilibrium*, which is completely specified by $\Delta S=0$ (it may be regarded as $\Delta S\simeq 0$, if it does not cause any theoretical confusion). However, a true thermodynamic equilibrium specified by $\Delta S = 0$ is considered as an ideal, ultimate state, or a mathematical construct, such as *heat death of the universe*, which is the hypothetical ultimate fate of the universe. Therefore, metastable equilibrium states should be flexibly interpreted by $\Delta S \simeq 0$. They are well known systems in reality; for example, the Sun in our solar system, planets and small solar bodies. Though the Sun's temperature T is very high, its entropy is low $\Delta S \simeq 0$ and metastable, whose state lasts for a long time. Thus, the variation of entropy ΔS is essential for the change of a thermodynamic state.

The typical thermodynamic quantity that is minimized at a metastable state is the Gibbs free energy:

$$G = \mathcal{E} + pV - TS, \tag{2}$$

where $\mathcal{E}, p, T, V$ and S are respectively the internal energy, pressure, absolute temperature, volume and entropy. By employing the Gibbs free energy, a metastable equilibrium state is completely defined by $\mathrm{d}G = -T\left(\mathrm{d}S_e + \mathrm{d}S_i\right) = -T\mathrm{d}S_i \le 0$, and $T\mathrm{d}S_e = \mathrm{d}Q$ at thermodynamic equilibrium and $\mathrm{d}S_i$ is a change in a nonequilibrium irreversible process [1]; $\mathrm{d}p = 0$ and $\mathrm{d}T = 0$ for closed homogenized systems. It indicates that heat-energy or entropy flows must progress as $\mathrm{d}S \to 0$, to thermodynamic equilibrium: $\mathrm{d}G = 0$.

As a specific model of a thermodynamically consistent theory, hot nuclear matter studied in the framework of *quantum hadrodynamics* is noteworthy [30]-[32]. The hadronic theory based on quantum hadrodynamics is a thermodynamically consistent relatvistic theory. General principles of Lorentz covariance and thermodynamic self-consistency are explicitly discussed and applied to relativistic many-body systems at finite temperature and density. The theory explicitly calculates $\mathcal{E}, p$ and S at temperature T and exhibits a metastable state of nuclear matter. Physical quantities explicitly maintain Gibbs' relation (2) in infinite nuclear matter. Hence, it is a rigorous theoretical system of reference to study properties of entropy variations for thermodynamically consistent many-body systems.

The variation of entropy should be written as: $\Delta S = S\left(T,V,N\right) - S_0$, and $\Delta S = 0$ can only indicate that $S\left(T,V,N\right) = S_0$ (constant), which simply asserts the physical fact that there exists a metastable state at a finite temperature T_0, whatever value the entropy $S\left(T_0,V,N\right)$ could be. The magnitude of entropy variation, $\Delta S = 0$ is more fundamental than that of $S\left(T,V,N\right)$. It is necessary to confirm that the physical process: $\Delta S\left(T,V,N\right) = 0$ faster than $T \to 0$ is not acceptable in thermodynamics, because the process induces a contradiction in terms of the concept of dynamics for heat-energy flow or entropy flow, which is not clearly explained in (1). Therefore, the eq. (1) should be written as:

$$\lim_{\Delta S \to 0} T\left(S,V,N\right) = T_0. \tag{3}$$

The statement (3) is always true for a metastable state. All thermal equilibrium states must be considered as metastable states expressed by:

$$\lim_{\Delta S \to 0} \Delta T(S,V,N) = 0, \tag{4}$$

where $\Delta T(S,V,N) = T(S,V,N) - T_0$ is used.

One should be very careful that the eq (4) declares the existence of a metastable state defined by a definite, constant temperature $T_0 > 0$ ($T_0 \neq 0$) with $\Delta S(T,V,N) \to 0$. The absolute temperature should not be a free parameter or a constant to be given arbitrarily in NISs. In other words, the variation $\Delta S(T,V,N)$ is more fundamental than that of temperature T, and the convergence to a uniform, constant temperature is obtained after the uniformity, $\Delta S(T,V,N) = 0$, is completed as a metastable state. Hence, the expression of (1) is physically inconsistent and ambiguous.

Based on the discussions so far, we suggest that the Nernst-Simon and Planck statements of the third law of thermodynamics and the unattainability of $T_0 = 0$ should be restated as:

[Remark 1]

A thermodynamic system with *definite value* of $T_0 = 0$ (K) simultaneously with $\Delta S(0,V,N) = 0$ is not possible.

The statement [Remark 1] expresses the unattainability of absolute temperature $T = 0$, and the Nernst-Simon and Planck statements of the third law of thermodynamics, $S(0,V,N) = 0$, is not appropriate nor necessary.

The unattainability of $T_0 = 0$ can be examined by the following mathematical principle of logic.

[Remark 2]

A metastable state defined by a positive $T_1 > 0$ can change to other metastable state by contacting with T_2 given by $T_1 > T_2$, and the metastable state T_1 advances to a thermal state T_3, resulting in $T_1 > T_3 > T_2$. In order to make T_3 less than T_2, a metastable system with the temperature $T_4 > 0$ ($T_2 > T_4 > 0$) has to be supplied to obtain: $T_2 > T_3 > T_4$. Similarly, one has to repeat the experiment and provide a metastable state with $T_n > 0$ (n designates a large number of supply) for cooling the system of T_3 to obtain: $T_4 > T_3 > T_n$. Ultimately, if one assumes to reach $T_3 = 0$, it must result in: $T_4 > T_3 = 0 > T_n$. This is a contradiction, since T_n less than the absolute temperature zero does not exist.

The process to attain $T_0 = 0$ through infinite time or infinite number of steps becomes a *self-reference* considered to be recursive, therefore, the proposed concept of the attainability $T_0 = 0$ is meaningless, *incomplete* and *undecidable* [33].

The discussions so far are essential to scrutinize the third law of thermodynamics and the unattainability of $T_0 = 0$ state. The consequence of [Remark 2] is fundamentally important, even if one employs the method of classical and quantum statistical mechanics. It must be understood that temperature is not an independent nor freely adjustable variable at the outset. The temperature is determined after uniformity of a system is achieved by $\Delta S = 0$. The entropy flow is the primary physical quantity to determine the temperature. The *nonequivalence of the Nernst-Simon and unattainability statements of the third law of thermody-*

namics [28] [29] hold true, and the requirement of the definite value of $S(0,V,N)=0$ is simply inappropriate, and the self-reference logical structure proves the unattainability of $T=0$.

The foundation of thermodynamics based on microscopic mechanical laws is one of the original aims of statistical mechanics, and all physical quantities are defined as *averaged* properties by the mathematical law of large numbers. The idea of entropy and probability distribution is introduced into thermodynamics by L. Boltzmann as $S(T,V,N)=k_B \ln W$; W is the number of microscopic states, and L. Boltzmann associated the number of microscopic states directly to thermodynamic entropy.

The Nernst-Simon and Planck statements of the third law of thermodynamics can be written by employing Boltzmann's idea as follows:

[Remark 3]

Let us denote $S(T=0,V,N)=k_B \ln W_0$ and $S(T>0,V,N)=k_B \ln W_1$. Then, one obtains,

$$\Delta S(T,V,N)=S(T,V,N)-S(T=0,V,N)=k_B \ln \frac{W_1}{W_0}. \tag{5}$$

If one takes the *microscopic assumption* that $W_1 \to W_0$ is true as $T \to 0$, then one obtains $\Delta S(T,V,N)=0$ with $T \to 0$.

In reality, the microscopic assumption is implicitly employed in proofs for the third law of thermodynamics, which means that temperature is taken as an independent variable. This is not correct because the variation of temperature is fundamentally restricted by entropy. The Nernst-Simon and Planck statements of the third law of thermodynamics assume that temperature T should change to 0 as a free parameter, however, absolute temperature T can be changed only if $\Delta S \neq 0$.

A. Einstein proposed that thermodynamic entropy should be defined from the probability of thermal fluctuation as:

$$P(\Delta S)=Z^{-1}\exp(\Delta S/k_B). \tag{6}$$

The formula relates probability of a fluctuation with entropy variations. The probability and assumption are tested to obtain the diffusion coefficient D_k and friction coefficient, known as the Stokes-Einstein relation [1]. A. Einstein opposed to the attainability of the absolute temperature $T=0$, which is now understood that putting a system into its ground state requires infinite time or infinite number of steps [34]. It is noticeable that the change of entropy $\Delta S(T,V,N)$ is used to obtain the probability of a fluctuation in a thermal state in (6), whereas the probability defined by the number of microscopic states is used to determine the entropy $S(T,V,N)$ in (5).

The unattainability statement in [Remark 3] becomes thermodynamically ambiguous, because the statement, $T=0$ as $W_1 \to W_0$, does not refer directly to the cause of the temperature variation $T \to 0$. The number of microscopic states W_1 is usually assumed to coincide with a thermal state at a homogeneous temperature T; however, this is closely related with classical or quantum measurement at a metastable state, the concept of reversibility, time and entropy. Thus, it should be emphasized that the entropy variation $\Delta S(T,V,N)$ is more fundamental than changes of temperature T and microscopic states W.

2.1. The Physical Interpretation of the Zeroth Law of Thermodynamics

In order to proceed discussions for the *zeroth law* and the *third law* of thermodynamics, it is essential to comment on the concept of entropy and temperature. As commonly explained in the text books in physics [1] [12], the zeroth law states that if two thermodynamic systems are both in thermal equilibrium with a third system, then systems are regarded as in a thermal equilibrium with each other and marked by a scale of temperature. In other words, if a body C, would be in thermal equilibrium with two other bodies, A and B, then A and B are in thermal equilibrium with each other. The systems only become homogeneous and indistinguishable from each other, but it is said that they are mutually marked and scaled by temperature, indicating that the zeroth law provides *an independent definition of temperature*. However, the statement that the zeroth law is an independent definition of temperature is not at all thermodynamically correct.

It is necessary to confirm that the zeroth law only suggests that it is impossible to distinguish a body C and other bodies, A and B, only when they are in *a metastable state* with the same homogeneous temperature or state. The thermodynamic systems must become an identical stable thermal state (a metastable state) before A, B and C are indistinguishable. A metastable state is completely defined by $\Delta S(T,V,N)=0$, and so, the zeroth law signifies the importance of entropy rather than temperature. The verification comes from the following argument:

[Remark 4]

Suppose that a body C is in thermal equilibrium with two other bodies, A and B, in thermal equilibrium with the same temperature T and it is not possible for an observer to distinguish systems. This is the definition of temperature in the zeroth law of thermodynamics. However, the systems, A, B and C, in thermal equilibrium with the same temperature T can be distinguished.

Let us conduct the experiment such that systems are in the state: A (solid), B (liquid), C (gas) with the same temperature T. The observer cannot distinguish systems in terms of temperature T but can distinguish systems A, B and C, because the phase and the entropies $S(T,V,N)$, of respective systems are different.

The result of the experiment proves that entropy is more fundamental than temperature, and the temperature T is exactly determined only after $\Delta S(T,V,N)\to 0$.

When A, B and C are in the same phase and temperature, an *internal observer* cannot distinguish the systems in terms of temperature. On the other hand, an *external observer* in a different metastable system can define with an available thermometer that the inner systems A, B and C are in the same homogeneous temperature T. It is possible to introduce the concept of temperature for internal systems, when the external observer is in a thermal state at different temperature. The existence of an external observer who already understands the scale of temperature makes it possible to determine temperature inside a homogeneous system. Even if systems become indistinguishable from each other and undetectable in terms of temperature, both the inside and outside observers can distinguish the difference of systems A (solid), B (liquid) and C (gas) in terms of entropy. Therefore, the zeroth law of thermodynamics only emphasizes that the concept of entropy is more important and fundamental.

2.2. Probabilistic Approaches, Classical and Quantum Statistics for Cooling a System

We continue discussing the Nernst-Simon and Planck statements of the third law of thermodynamics expressed as [Remark 1] and the unattainability of $T=0$ in terms of classical and quantum statistical method for entropies associated with Gibbs-Shannon-von Neumann entropies [35]-[37]. Thermodynamic states are considered to be coarse-grained microscopic states of quantum states for molecular, atomic energy levels and interactions. All microstates are assumed as equally probable and respectively corresponding to thermodynamic metastable states. Statistical thermodynamics uses ensembles related to a large collection of microstates of N identical particles or systems, and entropies defined by microstates and statistical mechanics are introduced to study macroscopic quantities at $T>0$. The classical and quantum statistics mathematically demand large numbers of systems and particles, infinite resources and heat baths, infinite processes and time needed to prove cooling a metastable state [38]-[40].

The key fundamental assertions in statistical and probabilistic approaches are the claim that cooling requires infinite processes and time, mechanical states, resources and heat baths, but the demand of infinity is replaced by the *large number hypothesis* to prove mathematically. The large number hypothesis in statistics are regarded physically sufficient for calculations. In other words, the method of mathematical induction is used to prove the existence of the $T=0$ state in the limit of infinity; however, the attainability of $T=0$ state produces the contradiction in terms of thermodynamics and self-reference structure, as shown in [Remark 2]. Hence, the absolute temperature $T=0$ state cannot be realized, and thermodynamic states T ($T\neq 0$) can be only meaningful. Any processes cannot reach absolute zero temperature in a finite number of steps within a finite time.

We emphasize that a finite temperature, metastable state $T\neq 0$ and the absolute temperature $T=0$ state are fundamentally different states to each other in the macroscopic, thermodynamic world. In other words, it should be understood such that the $T=0$ state cannot exist nor be true in the macroscopic thermodynamic world. Although a finite temperature, $T\neq 0$, metastable state is always possible and physical to realize, the absolute temperature $T=0$ thermodynamic state is nothing but a mathematical construct. This is clearly discussed in the method of TMD, in sec. 3.

2.3. The Physical Explanations for the Unattainability of $T = 0$ State

The statistical and mathematical discussions on processes of equilibrium states depend intrinsically on the large number hypothesis and the concept of mathematical infinity [39] [40]. The unattainability of $T = 0$ state is mathematically expressed as the necessity of infinite processes and time. Especially, the large number hypothesis and the proofs by employing mathematical infinity do not refer to the time-dependent variation of temperature. It would seem logically reasonable at thermal equilibrium, but it is macroscopically incorrect. The time-dependent temperature states $\tilde{T}(t)$ could be physically appropriate for dynamical systems as well as systems of *homeostasis*, abundant in nature. The time-dependent dynamical properties are produced from emergent processes of nonequilibrium thermodynamics.

The temperature in nonequilibrium processes changes in time and approaches a value slightly higher than the initial bath temperature which remains nonzero even for an assumed zero-temperature bath, and the conclusion suggests that a direct achievement of $T = 0$ from the process $T \to 0$ is physically questionable [41]. It is well known that processes and correlations among observables and systems give rise to memory effects or increases of information [42], leading to dissipations of heat and energy within the system-apparatus complex, known as entropy productions. In addition, the dissipations of heat and energy produce conservative and non-conservative quantities [43] subject to constraints coming from the second law of thermodynamics. Therefore, the physical meanings of the unattainability of $T = 0$ state is fundamentally related to emergent properties and processes of nonequilibrium thermodynamics.

In modern theories of measurement for quantum heat engines, work must be extracted from energy produced among microscopic mechanisms. Quantum measurements demand repeated energy exchanges among systems, apparatus and the broader external world, signifying that experimental measurements involve energy losses and dissipations. Certain portions of energy are transfered among systems and spontaneously dissipated into an environment or spent in recording the measurement outcome [44], and so, this is also subject to constraints coming from the second law of thermodynamics. Although the quantum measurement and interpretations of quantum mechanics at microscopic levels are not satisfactory resolved yet, they do not allow definite one to one correspondence between micro-macro states in experiments [45]. Moreover, an analysis of quantum measurement concludes that the third law of thermodynamics corresponds to the *unattainability of pure quantum states*. This is an important conclusion for quantum measurements to demand that the third law of thermodynamics should be definitely considered in conjunction with the first and the second laws of thermodynamics [46].

All modern technologies such as quantum computations, quantum simulations, manipulation of materials at atomic and molecular scales depend on precision measurements and experiments in extreme cooling so as to prevent thermal disturbances. The advancement of nano and micro scale science will continue to reconstruct energy productions from microscopic biochemistry to macroscopic computer technologies and so forth. Hence, modern quantum measurements are related to the extreme cooling technologies, and a solid understanding of electronics and heat-energy transfers at microscopic length together with thermodynamics and the concept of time are required [47]. However, tremendous increase of heat dissipations per unit volume associate with *miniaturization* technologies is a fundamental problem, and the technological constraint and the large number hypothesis lead to the unattainability of $T=0$ state.

Thermoelectric conversions and heat-energy transfers are abundant in our every day life, and heat engines from micro to macro devices have been proposed to extract thermomechanical work. The important theoretical fact is that systems of heat engines are all excellent experimental machines to investigate theories of nonequilibrium irreversible thermodynamics. Examples are abundant from macroscopic to microscopic scales such as, a drinking bird, a low temperature Starling engine, modern automobiles, jet engines and quantum heat engines [16]-[18] [48] [49]. The physical processes discussed in (3) with $T_0 \sim 0$ are connected to fundamental problems in various fields of science. In physics, the number of microscopic, quantum states and energy are fundamentally intertwined with thermodynamic time-dependent internal energy, entropy, work and heat-energy dissipations.

The Nernst-Simon and Planck statements of the third law of thermodynamics must be regarded as the statement of [Remark 1]. The entropy change $\Delta S(T=0,V,N)=0$ is more physical and important than the magnitude of entropy $S(T=0,V,N)$. The [Remark 2] proves that statistical and mathematical proofs of $T\to 0$ using infinite processes and resources would become self-referential, resulting in *incomplete* and *undecidable* [33]. The entropy productions and the unattainability of pure quantum states are inevitable [43]-[46], which signifies that the microscopic assumption of one to one correspondence of micro and macro states and the large number hypothesis in the [Remark 3] are intrinsically difficult to resolve in quantum measurement. The [Remark 4] concludes that the zeroth law of thermodynamics is for the concept of entropy and emphasizes that the entropy change $\Delta S(T,V,N)$ is more fundamental than the absolute temperature.

It is important to confirm that the zeroth law and the third law of thermodynamics should be considered as the auxiliary propositions or the corollaries and lemmas for understanding the second law of thermodynamics. The laws are fundamentally intertwined with the concept of entropy. It is noteworthy that the unattainability of $T=0$, or the cooling a system to $T=0$ with infinite resources and systems is considered to be a *self-reference process* as shown in [Remark 2]. The converging state of $T\to 0$ is only physical except $T=0$, and it would exhibit asymptotic states, depending on physical processes and nano-technologies to determine $T \to 0$. It signifies the measure of progresses of physics and technologies of precision experiments. The unattainability of $T = 0$ state is mathematically explained by the logical self-reference. The method of TMD precisely deduce the consequence of the unattainability of $T = 0$ in terms of thermodynamics. This is discussed in the next section.

3. The Method of Thermomechanical Dynamics (TMD) for Nonequilibrium Irreversible States

We proposed a model of thermomechanical dynamics (TMD) to study nonequilibrium irreversible states (NISs), and the method of TMD has consistently solved two independent problems of heat engines: a drinking bird and a low temperature Stirling engine. Thermomechanical motion and time-dependent changes of thermodynamic quantities, such as internal energy, thermodynamic work, heat dissipations (entropy flows) and temperature of heat engines are self-consistently solved in NISs. The phase transitions from thermodynamic equilibrium to NISs are consistently expressed in the TMD method, and thermodynamic functions are clearly studied in heat picture ($Q(t)$-picture) [15]-[18]. Moreover, the analysis of TMD has yielded a new technology of thermoelectric energy conversions, termed as a disk-magnet electromagnetic induction (DM-EMI) [25]-[27]. Therefore, we apply the consistent method of TMD to study physical meanings of the third law of thermodynamics and the unattainability, $T = 0$.

We explain the TMD method in a self-contained way for readers' sake. There are three propositions in the TMD.

1) The construction of the *dissipative equation of motion* for thermomechanical work.

The dissipative equation of motion for thermomechanical motion must be investigated by considering mechanical motion and phenomenological effects of frictional variations, time-dependent changes of physical parameters and mechanical components, thermal conductivity and efficiency for working fluid.

The dissipative equation of motion explicitly breaks time-reversibility and so, there is no Euler-Lagrange equation to construct the equation of motion, though Lagrangian or Hamiltonian method is very useful to find a possible dissipative equation of motion.

The mechanism of heat engines must proceed the *phase transition* from a metastable equilibrium state to NISs in order to extract thermodynamic work:

$$\Delta S(T,V,N) = 0 \;\rightarrow\; \Delta S(T,V,N) \neq 0 \tag{7}$$

and must perform the reverse process from NISs to a metastable equilibrium state:

$$\Delta S(T,V,N) \neq 0 \;\rightarrow\; \Delta S(T,V,N) = 0. \tag{8}$$

The thermodynamic states from (7) to (8) should be recurrently maintained for *cyclicity* of heat engines to derive thermodynamic work effectively.

The cyclicity is the key fundamental problem for macroscopic, thermomechanical states where thermodynamics, electromagnetism, classical and quantum mechanics simultaneously emerge. The phase transition from thermodynamic equilibrium to NISs is often expressed by the metaphor as the action of Maxwell's demon. The variation of entropy, the concept of Maxwell's demon, arrow of time and time-dependent physical quantities are all intrinsically intertwined as a fundamental principle of physics [45]-[50], and the TMD method will help understand interrelations among the fundamental dynamics.

The classical and quantum mechanical equations of motions are nonlinear differential equations with constant coefficients (NDE-CC) in which time-symmetry must be strictly maintained. However, the dissipative equation of motion in thermomechanical dynamics are nonlinear differential equations with *time-dependent coefficients* (NDE-TC) which must be time-asymmetric and express phase transitions from thermodynamic equilibrium to NISs [24]. The dissipative equation of motion with NDE-TC produces independent solutions which do not exist in NDE-CC. The independent solutions are termed as the bifurcation-integration solutions. The change from the time-symmetric equation of motion (NDE-CC) to the time-asymmetric dissipative equation (NDE-TC) is the genesis of thermodynamic time and phase transition phenomena.

The conservation law of heat-energy current regulates the dissipative equation of motion, which leads to the second proposition: the total heat-energy conservation law.

2) The total heat-energy conservation law at time t.

The time-dependent progress of thermodynamic work $\mathrm{d}W_{th}(t)$, internal energy $\mathrm{d}\mathcal{E}(t)$ and total entropy $T(t)\mathrm{d}\mathcal{S}(t)$ are assumed by the total heat-energy conservation law of thermodynamics as,

$$\mathrm{d}\mathcal{E}(t)/\mathrm{d}t = T(t)\mathrm{d}\mathcal{S}(t)/\mathrm{d}t + \mathrm{d}W_{th}(t)/\mathrm{d}t. \tag{9}$$

However, the conventional expression of thermodynamic energy conservation is inconvenient, because thermodynamic components are separately explained with mechanical energy (*Joule*) and heat energy (*Calorie*), which obscures fundamental differences between mechanical and dissipative processes.

The dissipative equation of motion, arrow of time and time irreversibility are intrinsically intertwined with phase transition phenomena. Thermomechanical motion fundamentally destroys information of initial conditions, and the arrow of time or the order of time appears naturally in thermomechanical systems. The time reversibility and even the possibility to run the equations of motion backwards in time (time-symmetry), is not at all a primary requirement in NISs. The direction and arrow of time would be uniquely defined in a thermomechanical system, even locally [50].

The Heat-Picture, $Q(t)$-Picture, and Proposition (3) in the TMD Method

In nonequilibrium thermomechanical processes, dissipations of entropy and energy occur simultaneously with those of thermodynamic work and internal energy (friction, viscosity among working fluid, wear and warming-up of internal systems, *etc.*). Therefore, in order to make discussions conspicuous, we rewrite internal energy as: $\mathcal{E}(t) = Q_\varepsilon(t)$, entropy flow or the total heat dissipation as: $T(t)\mathrm{d}\mathcal{S}(t)/\mathrm{d}t = \mathrm{d}Q_d(t)/\mathrm{d}t$ and thermodynamic work as: $W_{th}(t) = Q_w(t)$. The differential form of time-dependent total heat-energy flow (9) becomes:

$$\mathrm{d}Q_\varepsilon(t)/\mathrm{d}t = \mathrm{d}Q_d(t)/\mathrm{d}t + \mathrm{d}Q_w(t)/\mathrm{d}t, \tag{10}$$

This is the $Q(t)$-picture of the total heat-energy flow at time t, and thermodynamic equilibrium is connected as boundary conditions at the initial and final states. We refer to (10) as the total heat-energy conservation law at time t.

The $Q(t)$-picture (*calorie* unit) is helpful for theoretical investigations in NISs and consistently used in the analyses [15]-[18] and thermoelectric conversion devices using a disk-magnet electromagnetic induction (DM-EMI) [25]-[27]. We introduced a model for the heat dissipation and energy conservation in the $Q(t)$-picture [16] [18]. The heat flow of time-dependent thermal work $\mathrm{d}Q_w(t)/\mathrm{d}t$ and internal energy $\mathrm{d}Q_\varepsilon(t)/\mathrm{d}t$ must be separated into two constituent parts as the *thermally conserved* and *dissipating* parts. The concept of conserved and dissipated parts is important to realize thermomechanical, nonequilibrium processes, and all thermodynamic quantities are assumed to be separated into two parts as;

$$Q(t) = \text{thermally conserved energy} + \text{thermally dissipating energy}. \tag{11}$$

The decomposition is useful for studying a phase transition mechanism to NISs, and the analysis of NISs is readily tractable in the $Q(t)$-picture.

Hence, the time-dependent internal energy, $Q_\varepsilon(t)$ is separated as:

$$Q_\varepsilon(t) = Q_{\varepsilon i}(t) + Q_{\varepsilon d}(t). \tag{12}$$

The heat $Q_{\varepsilon i}(t)$ is the thermal internal energy, and $Q_{\varepsilon d}(t)$ is the associating heat dissipation. Similarly, thermodynamic work $Q_w(t)$ is separated as;

$$Q_w(t) = Q_{wk}(t) + Q_{wd}(t). \tag{13}$$

The heat $Q_{wk}(t)$ is the thermal kinetic energy, and $Q_{wd}(t)$ is the associating heat dissipation.

The total heat coming into a system is denoted by $Q_{in}(t)$, and the heat-energy conservation law is now rewritten as:

$$\begin{aligned} Q_{in}(t) &= Q_\varepsilon(t) + Q_w(t) \\ &= Q_{\varepsilon i}(t) + Q_{\varepsilon d}(t) + Q_{wk}(t) + Q_{wd}(t) \\ &= Q_{\varepsilon i}(t) + Q_{wk}(t) + Q_d(t), \end{aligned} \tag{14}$$

and the total heat dissipation is obtained by

$$Q_d(t) = Q_{\varepsilon d}(t) + Q_{wd}(t), \tag{15}$$

with $Q_d(0) = 0$. In $Q(t)$-picture, the direct expressions of non-equilibrium thermodynamic variables, such as pressure, volume, friction, stress, chemical potentials are suppressed. However, time-dependent internal energy $\mathcal{E}(t)$, thermodynamic work $W_{th}(t)$, the total entropy (heat dissipation) $Q_d(t)$ can be explicitly determined [25]-[27], and extended by including exchanges of particles and electromagnetic interactions.

The time-dependent thermodynamic progresses are founded with the propositions (1) and (2). The next fundamental problem is to establish the *measure* for NISs and phase transitions from a metastable equilibrium to NISs, which led us to the definition of time-dependent temperature, $\tilde{T}(t)$.

3) The definition of measure or the time-dependent temperature $\tilde{T}(t)$ in NISs.

The measure of a nonequilibrium irreversible state is defined by the ratio of entropy-flow against internal energy-flow:

$$\tau(t) = \frac{\mathrm{d}Q_d(t)/\mathrm{d}t}{\mathrm{d}Q_\varepsilon(t)/\mathrm{d}t}. \tag{16}$$

The value of $\tau(t)$ is a dimensionless, positive-definite function, $\tau(t) > 0$, and thermodynamic equilibrium is defined when the measure $\tau(t) = 1$ holds identically for all time [3]. This is proved by the conservation of energy (10) in the proposition (2) by requiring $\tau(t) = 1$, which generates the condition of thermodynamic equilibrium: neither thermodynamic work nor heat dissipation into an external system should exist in thermodynamic equilibrium.

The *time-dependent temperature*, $\tilde{T}(t)$, in NISs is defined by,

$$\tilde{T}(t) \equiv T_0 \tau(t), \tag{17}$$

where initial boundary conditions, $\tilde{T}(0) = T_0$ and $\tau(0) = 1$ are assumed at $t = 0$, and if a system converges to a metastable equilibrium after a sufficiently long time, the boundary condition, $\tilde{T}(t) \to T_0$, $\tau(t) \to 1$, should be introduced.

It is remarkable that the conditions of near equilibrium, local equilibrium defined by linearity of fluxes [1] [2] and time-dependent physical quantities of NISs are studied by the *near metastable condition*,

$$\tau(t) = \left(\mathrm{d}Q_d(t)/\mathrm{d}t\right) / \left(\mathrm{d}Q_\varepsilon(t)/\mathrm{d}t\right) \sim 1, \tag{18}$$

in the TMD model, which produced consistent results in heat engine analyses [15]-[18].

The measure or nonequilibrium temperature, $\tilde{T}(t) = T_0 \tau(t)$, reproduces empirically well-known results in applications, such as warming-up of heat engines, optimal fuel-injection timings, stability or instability of thermomechanical motion of heat engines [18]. The time-dependent thermodynamic quantities ($\mathcal{E}(t)$, $W_{th}(t)$, $\mathcal{S}(t)$, $\tilde{T}(t)$) in NISs, stability of a thermal state of heat engines, empirical results of the fuel-injection and combustion timings are numerically produced. The results have also contributed to construct new thermoelectric energy conversion devices for sustainable environmental technologies. The physical and mathematical concepts derived from the TMD method have established a physical approach for phase transition from a thermodynamic equilibrium to NISs and vice versa. Thus, based on the self-consistent and successful results, we apply the method of TMD to study physical meanings of the third law of thermodynamics.

4. The TMD Analyses on the Third Law of Thermodynamics

The TMD method is so far successful, classical thermodynamics to study thermo-mechanical systems, phase transitions from thermodynamic equilibrium to NISs. Thermodynamic properties in a metastable equilibrium state are specified by $\Delta S \simeq 0$, or $\Delta S = 0$, which is restated by the time-dependent temperature, $\tilde{T}(t) = T_0 \tau(t)$ in TMD. The method of TMD should be applied to the third law of thermodynamics to probe its physical meanings and implications.

A metastable equilibrium, $\tau(t) = 1$, results in $\mathrm{d}Q_d(t)/\mathrm{d}t = \mathrm{d}Q_\varepsilon(t)/\mathrm{d}t$, which suggests that a minute heat-energy fluctuation relation could internally exist in thermodynamic equilibrium, and one obtains: $\mathrm{d}Q_w(t)/\mathrm{d}t = 0$ from the time-dependent total energy-heat flow (10). Therefore, thermodynamic equilibrium is stated as:

[Remark 5]

Neither thermodynamic work nor heat dissipations into an external system should exist in thermodynamic equilibrium.

The near metastable condition, $\tau(t) \sim 1$ in the TMD method, is consistent with near equilibrium, local equilibrium condition defined by linearity of fluxes, which have been discussed in modern thermodynamic developments [1] [2]. Therefore, the physical meanings of temperature corresponding to the Nernst-Simon and Planck statements of the third law of thermodynamics and the unattainability $T = 0$ should be examined in the TMD model.

The system of thermodynamic equilibrium at the absolute temperature $T = 0$ is given by $\tilde{T}(t) = 0$, resulting in $\tau(t) = 0$. Then, as discussed in sec. 3, it results in:

$$\mathrm{d}Q_\varepsilon(t)/\mathrm{d}t = \mathrm{d}Q_w(t)/\mathrm{d}t. \tag{19}$$

The physical meaning of (19) is that thermodynamic work $Q_w(t)$ changes completely into internal energy $Q_\varepsilon(t)$ at $T = 0$ and vice versa. The result explains a contradiction that thermodynamic power $\mathrm{d}Q_w(t)/\mathrm{d}t$ exists without heat dissipations (entropy productions) and it violates the second law of thermodynamics. The metastable state with absolute zero temperature $T_0 = 0$ and $\Delta S(T_0, V, N) = 0$ is fundamentally different from a metastable state defined by $T_0 > 0$. Therefore, the state $T = 0$ does not exist as a macroscopic, thermodynamic state, which is clearly declared in the TMD approach.

The infinite processes and resources to achieve the $T = 0$ state are completely rephrased such that the $T = 0$ macroscopic thermodynamic state does not exist because of the violation of the second law of thermodynamics. The processes to produce metastable states, $\Delta S(T, V, N) \to 0$ and $T \to 0$, are always physical; however, the state of the mathematical limit, $T = 0$ and $\Delta S(T, V, N) = 0$, never exists as a metastable state in the macroscopic, thermodynamic world.

The thermodynamic temperature with values of $\tau(t) > 1$ progresses to a metastable state from above, $\tilde{T}(t) \searrow T_0$, and the Sun in our solar system is a typical example. The thermodynamic temperature with values of $1 > \tau(t) > 0$ progresses to a metastable state from below $\tilde{T}(t) \nearrow T_0$ [15], and typical examples are the solid-liquid and liquid-gas phase transitions of water. The temperature $\tilde{T}(t)$ (16) is consistent with empirical results of heat engines, such as stability, time-dependent changes of thermal states, ignition and detonation phenomena of heat engines [25]-[27]. The thermal state ($T = 0$) can be only discussed as a mathematical construct of a limit value. The recognition of the concept is fundamentally important to understand macroscopic thermodynamics as well as nonequilibrium irreversible thermodynamics. It should be emphasized that the *unattainability* of $T = 0$ state is not because it is difficult to achieve, but because the thermodynamic system at $T = 0$ should never exist.

5. The Arrow of Time, Thermodynamic Measurement and Quantum Measurement

The third law of thermodynamics and the unattainability of the absolute temperature $T = 0$ have guided us to study profound theoretical problems in the course of investigations. Thermodynamics has coevolved with the vast fields of science from atomic and molecular interactions, self-organizations of cells to modern technologies of jet engines, thermal and nuclear power stations. Following the course of discussions in the current paper, we discuss profound interrelations among the variation of entropy $\Delta S(T,V,N)$ in NISs, thermodynamic and quantum measurement, and emergence of the arrow of time.

The measurement of temperature is recorded according to a sequence of time from the beginning of an experiment to an end, and a thermodynamic system evolves from a metastable state to a time-asymmetric NIS and then, to a metastable state: $\Delta S(T,V,N) \to 0$ at a temperature T_0. This induces the *arrow of time* as required by *causality* which makes an ordering of events possible from the past to the future, and the past should not depend on the future. One should notice that there exists no concept of time (internal time) in a metastable state to distinguish the past and the future because of the time-symmetry in thermodynamic equilibrium. The passage of time in a thermodynamic, macroscopic state is defined only by *external* observers who are in an external nonequilibrium system where time-symmetry is broken and *irreversible in time* [50]. The *concept of time* in nonequilibrium thermodynamic states is intrinsically different from the time of classical and quantum mechanical systems.

The basic equations of motion in classical and quantum mechanical systems are reversible in time, signifying that motion can go backwards in time as it can go forwards in time, however it is never reversible in nonequilibrium irreversible states (NISs). For clarity, it should be emphasized that the technical terms, such as time-symmetry, reversibility in state, $\Delta S(T,V,N) = 0$ and the measure $\tau(t) = 1$ express the same property of metastable states. Similarly, the arrow of time, causality and ordering of time, time-asymmetry and spontaneous changes of states, and the measure $\tau(t) \neq 1$, are equivalently regarded as the *tautology* of the property of NISs. This is essential to avoid needless repetitions of the same property for NISs and clearly understand phase transitions from thermodynamic equilibrium to NISs, time-dependent entropy $\Delta S(T,V,N)$ and temperature $\tilde{T}(t)$.

Before discussing the progress and variation of events in a thermodynamic system, the difference between *internal* and *external* time should be clearly explained. The concept of time appears according to the (internal) variation of entropy $\Delta S(T,V,N)$, and thermodynamic time is induced as *internal* time. The examples for systems of internal time are abundant in living systems of animals and plants. They are approximate metastable systems with self-sustaining processes, which respectively have their own life time. On the contrary, nothing can be ordered in a system of thermodynamic equilibrium; therefore, only the existing observers in external NISs can define the magnitude of time sequences (seconds, minutes, …) as the external observer. It is important to realize that there is no concept of time inside the system of thermodynamic equilibrium.

Entropy is the property of physical variations of a macroscopic state, and temperature expresses the property of a metastable system, determined at the end of the last homogeneous, macroscopic system. Any nonequilibrium states will evolve to thermodynamic equilibrium $\Delta S(T,V,N) \to 0$ together with time, and the absolute temperature is precisely determined after homogeneity of a system, $\Delta S(T,V,N) = 0$, is reached, discussed in detail in conjunction with physical meanings of the zeroth law of thermodynamics in [Remark 4]. A system progresses to a metastable equilibrium state with time which disappears when a system of thermodynamic equilibrium is reached, because an equilibrium state becomes time-symmetric and it is impossible to do ordering of events inside the metastable system. The time sequences defined by entropy and mechanics are essentially different quantities. The difference of the time concept should be clearly understood to avoid fundamental misunderstanding and discussions.

The analysis of evolution to thermodynamic equilibrium in terms of $\Delta S(T,V,N)$ makes one to realize that one must be careful to distinguish an *internal observer* from an *external observer*, since one cannot distinguish systems if the observer itself would be one of A, B or C [see, Remark 4]. For example, it might be explained such that we usually would not recognize quality and temperature of air we breath. If the temperature or the entropy of air is too high or low, we immediately recognize what happened in time. The reason why we can distinguish systems and measure time is because we can recognize the entropy difference or the order of things around our environment as independent observers. Similarly, an *external observer* who already understands the concept of time and temperature can measure them and observe that the inner systems A, B and C are in the same homogeneous temperature. However, it is not possible for an external observer to distinguish the system A, B and C in terms of temperature, but the system can be distinguished in terms of entropy by an internal observer. The logical consequence signifies the importance of entropy and the fundamental relation between the variations of entropy $\Delta S(T,V,N)$ and the arrow of time.

Now, one can understand how important to realize time in the proposition (1) of the TMD method; the time-variable begins to appear starting from constructing the dissipative equation of motion. The dissipative equation of motion is a nonlinear differential equation with time-dependent coefficients (NDE-TC), which is not derived from Euler-Lagrange equation of classical and quantum mechanics. This is fundamentally different from a nonlinear equation of motion with constant coefficients (NDE-CC), derived from Euler-Lagrange or Hamiltonian methods. The noteworthy properties of the dissipative equation of motion are: 1) time-dependent phase transition solutions from thermodynamic equilibrium to NISs and vice versa are found in NDE-TC; 2) independent solutions that do not exist in the equation of motion derived from Euler-Lagrange or Hamiltonian methods can be discovered in NDE-TC [24]. This is because the time in the dissipative equation of motion is induced by changes of states, frictional thermomechanical motion and heat-energy flows.

The conservation of the total heat-energy flow is defined in the proposition (2), and the time-dependent dynamical quantities have been discussed by employing heat engines, such as motions of a drinking bird, a low temperature Stirling engine [18] and a rotary engine, resulting in vast applications in renewable, technological devices in thermoelectric generations [25]-[27]. The empirical phenomena, such as ignition, warming-up of engines, stable rotational motion and stalling of engines are precisely shown by time-dependent $\tilde{T}(t)$. The measure (time-dependent temperature $\tilde{T}(t)$) defined in the proposition (3) maintains thermodynamic consistency at time t. The time-dependent variations of internal energy $\mathcal{E}(t)$, thermodynamic work $W(t)$, dissipation of heat $Q_d(t)$ or entropy $\mathcal{S}(t)$ and nonequilibrium temperature $\tilde{T}(t)$, are consistently produced in the TMD approach. The appearance of time-variable signifies the *phase transition* from thermodynamic equilibrium to NISs, and the phase transition is essentially created and interrelated with a time-dependent physical constant in NDE-TC. The time-evolution of thermodynamic potentials becomes stable and time-independent as the system reaches a metastable state.

A quantum measurement involves energy exchanges among systems to be measured and measuring apparatuses. Dissipations of heat and energy within a system-apparatus complex cause entropy productions and non-conservative quantities [41]-[43]. Some of heat and energies are dissipated into the environment or used in recording the measurement outcome [44]-[46]. Therefore, the variation of entropy $\Delta S(T,V,N)$ and the arrow of time fundamentally distinguish thermodynamic *macroscopic world* from quantum mechanical *microscopic world*. The finite temperature $T \to 0$ (but $T \neq 0$) is always consistent in the thermodynamic world however small value it is, and a thermodynamic system progresses to a metastable state. If one assumes that thermodynamic state $T = 0$ exists, it immediately becomes inconsistent with thermodynamics itself as discussed in TMD. Although the convergence of $T=0$ state could be mathematically defined, it is only realized as the limit of asymptotic state in the macroscopic, thermodynamic world.

6. Conclusions and Perspectives

Based on the criticisms in sec. 2 and the analysis in the TMD approach, we conclude that the third law of thermodynamics, the unattainability of $T=0$ and the zeroth law of thermodynamics are essentially interrelated with the concept of entropy variation, $\Delta S(T,V,N)$, which is intrinsic in the second law of thermodynamics. Therefore, the zeroth and the third laws, the unattainability of $T=0$ should be rather considered as the essential, theoretical problems to understand the concept of entropy $S(T,V,N)$ and entropy variation $\Delta S(T,V,N)$. The concept of temperature and the unattainability of $T=0$ are clearly explained in the physical and mathematical context of the first and the second laws of thermodynamics. Therefore, the first and the second laws of thermodynamics suffice as the fundamental laws of thermodynamics.

The time-dependent temperature $\tilde{T}(t)$ obtained by TMD has been consistent with empirical results of heat engines, and it is very useful to study fuel-injection and combustion timings, stability and changes of thermal states and diffusion mechanisms. The result suggests that temperature expresses how slowly or violently, an internal thermal state responses against external heat flows. This is a new physical interpretation for temperature [18]. It should be understood that temperature T is precisely determined in a metastable system, $\Delta S(T,V,N)=0$. Therefore, the unattainability of $T=0$ is directly related to entropy productions, the non-conservation of thermal energy by dissipations; hence, the $T=0$ state demands infinite time, infinite resources and processes. The mathematical proof of the unattainability of $T=0$ state is confirmed by showing the logical self-reference structure to attain $T=0$ state. The TMD method directly concludes that the metastable $T=0$ state is inconsistent as a thermodynamic system, since the $T=0$ state corresponds to that of $\tau(t)=0$, which does not exist in our thermodynamic world.

The concept of time does not exist inside a metastable system, because symmetry of time, causality and ordering of time are not maintained inside the system. However, an observer outside the metastable system can measure time, assuming the time in a metastable system is passing by as defined by the external observer's time. The *external* observer's thermal state and time are changing, but nothing is changed inside a metastable system. Hence, it is essential to understand the physical difference between mechanical and thermodynamic time. The time progressions in TMD is induced by the time-dependent dissipative equation of motion (NDE-TC), which is succeeded to dynamical quantities and the measure $\tau(t)$ by way of the conservation of heat-energy flow discussed in sec. 3. The time variations of internal energy $\mathcal{E}(t)$, thermal work $W(t)$, entropy $\mathcal{S}(t)$ and nonequilibrium temperature $\tilde{T}(t)$ appear simultaneously with phase transitions from thermodynamic equilibrium to NISs.

The fundamental mechanism of quantum mechanical technologies such as atomic clocks is conveniently used to define universal time sequences in human society. The internal arrow of time independently appears in a metastable system with a characteristic ordering of time caused by the time-variation of entropy. It should be emphasized that the *internal time* should not necessarily be identical to the external time sequences. The explicit examples of internal times are empirically observed in biological systems as varieties of lifetimes of living beings. Therefore, the variation of entropy $\Delta S(T,V,N)$ and a characteristic arrow of time simultaneously emerge in phase transitions to NISs.

The nonequilibrium irreversible thermodynamics is evolving to a fundamental theory by unifying and supporting Newtonian mechanics, electromagnetism and quantum mechanics. The investigations of the zeroth and the third laws of thermodynamics in terms of TMD helped clarify fundamental physical relations among entropy, temperature and the arrow of time. The laws of physics and sciences in general are helpful to understand the natural world with generality and simplicity, which provides us with a possible maximum knowledge produced from a minimum basic laws and concepts. The scientific way of logical procedure should be checked to trust its validity, but it is difficult to understand logical and technical consequences of scientific knowledge, since knowledge has been gained by trial and error in the process of theoretical and technical progress. Thermodynamics and its extension to NISs certainly have helped science and enlightened the concept of existence and dynamics of the macroscopic, thermodynamic world. The analysis in the current paper reminds us of a profound notion: Science has no final form and is moving away from a static geometrical picture towards a description in which evolution and history play an essential role [1]. It would be interesting to apply TMD to the problem of *Maxwell's demon* to extend and clarify the concept of NISs and phase transitions from thermodynamic equilibrium to NISs, which will be investigated in the near future.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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