Residual Entropy of Glasses and the Third Law Expression

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Abstract. The third law of thermodynamics dictates that the entropy of materials becomes zero as temperature ($T$) approaches zero. Contrarily, glass and other disordered materials exhibit nonzero entropy at $T = 0$, which contradicts the third law. For over a century, it has been a common practice to evade this problem by regarding glass as nonequilibrium. However, this treatment causes many inconsistencies in thermodynamics theory. This paper resolves these inconsistencies and provides a rigorous expression of the third law without any exception. To seek the entropy origin, the anthropomorphic feature of entropy must be resolved. Because entropy can be uniquely determined only when thermodynamic coordinates (TCs) are specified, we have to identify these TCs. For this purpose, the equilibrium for solids should be clearly defined such that it does not depend on solid structures. On this basis, it is deduced that TCs of solids are the equilibrium positions of atoms. TCs comprise a thermodynamic state space, on which a unique value can be assigned to entropy. For solids, equilibrium states are specified by discrete points in the thermodynamic state space, which define atom configurations. Among various atom configurations, only one is thermally activated at sufficiently low temperatures, which is the equilibrium state at $T = 0$. Other atom configurations are called frozen configurations, which do not contribute to the temperature dependence of entropy near $T = 0$. The rigorous statement of the third law has been established by expressing that the entropy associated with the active configuration vanishes at $T = 0$. Residual entropy arises when the entropy is evaluated on an extended state space including the frozen configurations, which were previously active at high temperatures. The reconciliation of the two different views is explained through several debates on the glass transition.
1. Introduction

Historical background. There are no other laws in physics than the third law of thermodynamics that invoked much controversy and yet lacks a consensus. The third law is known as the Nernst heat postulation, which claims that the entropy ($S$) of materials vanishes as temperature ($T$) approaches absolute zero. However, there are exceptions to this law. Some of asymmetric diatomic molecular crystals, ice crystals, and solid solutions have indeed nonzero entropy at $T = 0$. The nonzero entropy at $T = 0$ is called residual entropy, $S_{\text{res}}$. Studies in early days are well documented in textbooks [1–6]. A law allowing exceptions cannot be a physics law. A thorough explanation is required for the existence of exception. In a day, it was claimed that the validity of the third law should be restricted only to chemically pure crystals. This restriction is meaningless. Silicon crystal is chemically pure yet it has residual entropy due to its isotope distribution. On the other hand, many compound crystals have vanishing entropy at $T = 0$, although they are not chemically pure. The residual entropy due to the mixing of different elements, which is observed in all random alloys, is a challenge for the third law since its discovery [7].

Among these counterexamples, the most important and thereby most widely studied material is glass [8]. After extensive studies on glass in the early of 20th century, Simon concluded that glass is not in the equilibrium state below the glass transition temperature ($T_g$) and thereby is exemplified from the laws of thermodynamics [9, 10]. He held the view that thermodynamics laws must be reserved for only equilibrium states [11]. Since then, the view of the nonequilibrium nature of glasses has prevailed [12]. However, this explanation does not address all concerns. Now, we know that residual entropy stems from freedom in atom configurations, which exists in any imperfection. Because no crystal is defect-free, we can say that no crystals obey the third law. Applying the explanation used for glass to other materials, therefore, leads to the absurd conclusion that all crystals must be in nonequilibrium states. In addition, many materials, such as incommensurate crystals, quasicrystal, and frustrate systems having ambiguous structures were discovered, as the material research was developed. It is unclear whether these materials are nonequilibrium states or not.

The view that the current state of a glass is a nonequilibrium state is rationalized by regarding that the glass will be crystallized or transform into an “ideal” glass, which has no residual entropy, given enough time. However, there is no experimental evidence to support this. Instead, there are many pieces of evidence that glasses do not change over more than million years [13, 14], as discussed in Sec. 2. Similarly, it is also said that random alloys will be eventually transformed to ordered compounds over time, yet this view also lacks experimental evidence. An extreme example is the random distribution of isotopes, where no one can imagine that isotopes will spontaneously organize into an ordered arrangement. Relying on such uncertain expectations is not advisable when a fundamental law is constructed. Furthermore, it is questionable to assume that the equilibrium state of materials is always an ordered form. Frustrated systems have no
ordered form. For quasicrystal and DNA, it is unclear even what the order means. Maybe an explanation different from the glass case is required. However, such case-by-case explanations lose our trust in the third law. Thus, some researchers questioned the validity of the third law [15–24] and even abandoned it from fundamental laws.

Despite the above difficulties, there is a compelling reason to defend the third law. There is another expression for the third law, that is, the unattainability of absolute zero temperature. In this respect, the third law turns to be a universal law without any exception, irrespective of whether the system is in equilibrium or not. This unattainability cannot be deduced from other laws of thermodynamics, making the third law indispensable. Fowler and Guggenheim exploited the unattainability of absolute zero temperature to deduce the rigorous expression for the Nernst heat postulation that does not allow any exceptions [1]. In a primitive sense, their third law expression is correct, if the frozen state is suitably interpreted [25]. Several studies have investigated whether the two expressions, the Nernst neat postulation and the unattainability of the absolute zero temperature, are equivalent or not [15–17, 19, 26–29]. Hatsopoulos and Keenan pointed out that their equivalence cannot be proved when the residual entropy is involved ( 26, p. 29 in Foreword). Without resolving the residual entropy problem, the proof for this equivalence is incomplete [30].

Recently, debates on the residual entropy have been revived, in connection with more subtle problems of glass. Some computer simulations and thermodynamic considerations showed an uncompensated decrease in entropy at the glass transition, which will lead to zero entropy at \( T = 0 \) [31–33]. These studies defend the third law. However, then why residual entropies are observed in experiments must be answered. Kivelson and Reiss ascribed this contradiction to the problem of calorimetric measurement. The entropy change \( \Delta S = S_B - S_A \) from state \( A \) to \( B \) is obtained by the calorimetric method,

\[
\Delta S = \int_A^B \left( \frac{dQ}{T} \right)_{\text{rev}}
\]

where the subscript (rev) indicates that the integration must be taken along a reversible path. The glass transition is generally an irreversible process, and, according to them, the obtained calorimetric value does not reflect the true value of entropy [31]. This invoked serious debate [34–42]. Another important issue in the debate is an uncompensated reduction of entropy. This means the spontaneous reduction of entropy, which contradicts the second law of thermodynamics. Gupta and Mauro evaded this contentious problem in terms of a human intervention of observation: the glass transition occurs only because our observation time is finite, and the act of observation serves a constraint that is not treated within the thermodynamic laws [43].

Regarding the reality of residual entropy, the debate seems to settle on the conventional view that the residual entropy is real. However, we must not ignore the logical inconsistency in ascribing the residual entropy of glass to a nonequilibrium state. If glass were in a nonequilibrium state, speaking of residual entropy itself would become meaningless. The residual entropy is measured by the calorimetric method,
which assumes equilibrium. No one ever solved this fundamental self-contradiction. In this way, the third-law issue is fallen into a deep impasse.

Contentions. The problem of residual entropy has been reiterated for over a century without any solution. By deeply analyzing the failures of previous explanation of the third law (further details of the failures are described in the early version of the manuscript [25]), the author came to find that the problems stem from the ambiguous understanding of equilibrium. Researchers repeatedly mentioned the nonequilibrium feature of glasses. However, in the thermodynamics context, equilibria can be measured using temperature: the zeroth law states that all the states of substances are connected by the relation of equilibrium when they have the same temperature. The temperature of glass is, of course, measured with no difficulty. This is by no means a trivial matter. On the other hand, we will find, in the literature, no rigorous definition of equilibrium that does not involve self-contradiction, as discussed in Sec. 2. The issue of residual entropy cannot be solved without tracing back to the definition of equilibrium.

Another issue related to the equilibrium is the notion of state variable. There is arbitrariness in entropy [44, 45], which is called the anthropomorphic feature of entropy [46] (first used by E. P. Wigner). A paramagnetic salt is in an ordered state when the crystal structure is studied, and hence \( S_{\text{res}} = 0 \). However, when magnetic properties are studied, the residual entropy appears due to random orientations of spins. This arbitrariness must be eliminated; otherwise, the entropy origin cannot be uniquely determined. A thermodynamic relation,

\[
dS = \frac{1}{T}dU - \sum_{j=1}^{M} \frac{F_j}{T}dX_j,
\]

(2)
tells us how the state variables \( X_j \) are related to the entropy change (\( U \): internal energy, \( F_j \): the generalized force conjugate to \( X_j \), \( M \): the number of variables). Accordingly, it is crucial to clarify concrete state variables for solids. For gases, it is true that only two variables, temperature \( T \) and volume \( V \), are independent state variables. (Here we consider only systems of one chemical component.) Most researchers hold the same answer for solids too. However, this is not obvious. Clear definition of state variables is unavoidable. Henceforth, we use the term thermodynamic coordinates (TCs) for state variables as “coordinate” is a suitable word for mathematical description [47].

Purpose. By studying residual entropy, the present study aimed to establish an unambiguous statement of the third law. The present paper is a substantially revised version of earlier studies [25, 30]. As mentioned above, the critical issue for the residual entropy is the understanding of equilibrium and TCs in a consistent manner, which was not fully achieved in the early studies. The rigorous definitions of equilibrium and TCs are given in author’s another study [48], which is an extension of the theory of Gyftopoulos and Berreta [49] to solids. Here, the unambiguous expression of the third law is constructed by starting from the rigorous definitions of equilibrium and TCs.
Historically, many fundamental problems about the third law were discussed through the glass issues, and accordingly the glass issues are thoroughly addressed throughout this paper. The rigorous definitions of equilibrium and TCs adapted here are so novel from the conventional understanding that readers might be concerned about the validity of the present theory. This theory has, however, received growing acceptance through previous studies on glass: the glass state [50], the hysteresis in glass transition [51], the activation energy of transition [52], and specific heat jump [53], which constitute the background of the present study. The investigation of the residual entropy of glass is now in order.

This paper is organized as follows. In Sec. 2, the rigorous definition of equilibrium is given. In Sec. 3 the definition of TCs is given along with some of relevant notions. In particular, the notion of frozen coordinates is critical to understanding the anthropomorphic feature of entropy. The essential parts of Secs. 2 and 3.1 were already given in a previous study [48]. However, the third law is so fundamental that it is difficult to give satisfactory explanation without logical completeness, and hence, they are included here with some rearrangements. Based on this foundation, we develop an appropriate expression for the third law in Sec. 4. In Sec. 5 we address several intriguing discussions concerning residual entropy at the glass transition temperature, thereby demonstrating the advantage of this study. In Sec. 6 the main results are summarized.

2. Equilibria in a solid

2.1. Definition of equilibrium

Defining thermodynamic equilibrium (or shortly equilibrium) is challenging (in Ref. [54], Sec. 1.5). We know that thermodynamic equilibrium is characterized by a few TCs. However, what are TCs? We may answer that TCs are macroscopic properties characterizing the equilibrium. But, the formers have sense only in the latter, and thus the argument becomes circular [55]. Only a way to escape from this circular argument is to start outside equilibrium and to treat equilibrium as a special case of nonequilibrium. This is the approach that Gyftopoulos and Beretta (GB) employed to establish a consistent theory of thermodynamics [49]. They placed the second law at the starting position of thermodynamics. Only the second law is more fundamental than the fundamental notion of equilibrium: a fundamental notion cannot be deduced from less fundamental laws. The GB approach is general, irrespective of the type of substance, gas or solid (a brief exposition of the GB approach is given in Supplemental material; however, for deeper understanding, refer to the original work [49]). However, GB did not show how to apply their theory to solids. This is not at all a trivial task. As described in Introduction, in the real world, every crystal has imperfections. Sometimes it is claimed that defect states of a crystal are meta-stable whereas the perfect crystal is the most stable state. However, it is our leaning from elemental thermodynamics that the
equilibrium concentration of the defect is determined by the condition of the minimum in the free energy. In this sense, the perfect crystal is nonequilibrium. Furthermore, there are a class of materials having ambiguous structures, such as frustrated systems. For them, it is difficult to say equilibrium. We have to reappraise the definition of equilibrium.

Let us begin to consider a system consisting of many particles. The system is generally in a nonequilibrium. A nonequilibrium state is characterized by a set of time-varying (dynamical) variables $X(t)$: any physical quantity determined by well-defined measurements is a dynamical variable. The number of particles in a small segment of space, $n(r, t)$, is an example. Suppose that the system is adiabatically connected to a weight as the sole device external to the system.

**Definition 1: Thermodynamic equilibrium**

*It is impossible to change the stable equilibrium state of a system to any other state with its sole effect on the environment being a raise of the weight.* [GB, p. 58]  
The statement of its sole effect on the environment being a raise of the weight means in usual terms that work can be extracted from the system without leaving any effect on the environment. If two systems $A$ and $B$ are in relation of equilibrium, contact of $A$ and $B$ does not cause any change in their states. If these two are not in equilibrium, the contact causes a spontaneous change, yielding entropy production. The maximum work theorem states that an increase in entropy can be converted to the net work on the environment, if an appropriate thermal engine is inserted. If a system has hot and cold regions, heat flows from the hot to the cold region, from which the net work can be obtained. After reaching the homogeneous distribution of $T$, work is no longer obtained. The equivalence of the temperatures of two regions that are in equilibrium with each other agrees with the zeroth law of thermodynamics.

From Definition 1, it is concluded that all the existing crystals are in equilibrium states, because we cannot extract work from the crystal without affecting the environment. Glass is no different from crystals in this respect. If work were obtained from a glass without affecting the environment, this would violate the second law. The equilibrium characterization of glass is the direct result of Definition 1. In material science, it is generally thought that glass is in nonequilibrium. One reason that they consider is the sluggish change in the glass structure. This aspect is discussed in the next subsection about timescale. Another reason is that the current properties of a glass cannot be expressed by the current value of $T$ and $V$ solely, as described in Introduction. However, that only $T$ and $V$ are independent TCs for solids is not true. This is the main topic of Sec. 3. Furthermore, it is often claimed that the glass state is less stable than the supercooled liquid at $T < T_g$. This is never supported by specific heat measurements [50]. Within the context of thermodynamics, Definition 1 solely represents the equilibrium concept, which is independent of material’s internal structures.
2.2. Constraint, timescale, and ergodicity

**Constraint.** Definition 1 presumes fixed constraints. A gas distributed homogeneously in a cylinder with a piston is in equilibrium, provided that the piston is constrained to fix. However, if this constraint is relaxed, work can be obtained. The definition of equilibrium is valid only when constraints are imposed. In the case of the cylinder plus the piston, it is obvious that the constraints are the their walls, which specify the volume \( V \) of gas. However, inside materials, the notion of constraints is clouded.

The idea of constraints in materials was introduced by Gibbs more than a century ago [56]. He used the word passive resistance. His intention was to distinguish two categories in static states. One case is static state that is achieved by the balance of the active tendencies of the system. There is another case of static states in which any change in the state is prevented by passive resistances. Paraffin oil is stable at standard temperature and pressure, and the paraffin oil and air are in equilibrium. A constraint that inhibits the chemical reaction is at play. The nature of constraints was not known at the age of Gibbs, which is now perceived as an energy barrier. The energy barrier suppresses the reaction rate to such a low value that the reaction is almost completely inhibited. A passive resistance is a perfect inhibitor, contrary to its modest name [26]. In the present context, however, there is no need to distinguish the above two categories of equilibria. Both macroscopic walls and microscopic energy barriers in materials are constraints.

**Definition 2: Constraint**

A constraint \( \xi_j \) is a means of restricting the range in which a particular variable \( X(t) \) can vary.

It is expressed by either a hypersurface \( \xi_j(X(t)) = 0 \) or a range \( \xi_j(X(t)) > 0 \). Although the restriction can be applied to any mode of change, we restrict, in this paper, ourselves to those in the real space. For a solid, atoms cannot move beyond the unit cell that each atom belongs. The boundary, \( \xi_j \), of the \( j \)-th unit cell for the \( j \)-th atom plays the role of a constraint. However, a more realistic substance of the constraint in this case is the energy barrier \( E_{b,j} \) which surrounds the \( j \)-th atom. A crystal retains its own structure by a set of constraints that every atom in the crystal is subjected to. This is also true for nonperiodic materials. In this respect, the structure is akin to a constraint, which identifies a given type of solid from others. In the glass literature, a special terminology of kinetic constraints is often used [57,58]. This terminology is an artificial device in order to make thermodynamic analysis amenable. In this study, constraints are real substances that refer to energy barrier inside materials.

**Timescale.** Any equilibrium is subjected to timescale. An equilibrium is sustained by the given constraint \( \xi_j \) that inhibits the change of the \( j \)-th type in the structure. The substance of a constraint is the energy barrier \( E_{b,j} \) for the \( j \)-th type change. Real barrier heights are always finite, no matter how high it is. This brings about a finite time of relaxation \( \tau_j \) in which the constraint effectively works. Therefore, the timescale \( \tau_j \) of
equilibrium is controlled by the energy barrier $E_{b,j}$ as

$$1/\tau_j = \nu_j e^{-E_{b,j}/k_B T},$$

where $\nu_j$ is an appropriate trial frequency and $k_B$ is Boltzmann’s constant.

An often-claimed reason for the nonequilibrium feature of glasses is that, if we wait for a long time, the glass will be crystallized. This is a speculation for future events. Nobody observes the crystallization of glasses. Moreover, the fact about glass is at variance with this speculation. The current observation is that glasses can maintain their structures more than a million years [13]. Alternatively, most metals degrade due to corrosion, oxidation, and other effects within a thousand years. This is the reason why glass is used for the capsule materials in nuclear wastes. Thermodynamic considerations for this stability problem are given in Refs. [50,51]. Previous interpolation schemes, such as the Vogel-Fulcher-Tammann law, that predict long-term structural changes are now not supported by recent experiments, which took good care of the timescale [14,59–61]. It is inappropriate to use logically inconsistent arguments for constructing fundamental laws, and accordingly we do not use the nonequilibrium assumption for glass in the following.

**Ergodicity-breaking process.** Equilibrium means ergodicity. Ergodic state is understood as the state that every particle in a system visits everywhere in the system with equal probability. However, this equal probability is often misconstrued, when constraints lead to the disruption of equal probability. Penrose noted that, for nonergodic systems, the energy manifold can be partitioned into invariant submanifolds ([62], p. 1947). It is often stated that the glass transition is an ergodicity-breaking process. However, every crystallization process is an ergodicity-breaking process: every atom is so constrained that it cannot move beyond the unit cell to which it belongs. Crystals are the most ergodicity-breaking systems, and yet they are in equilibrium.

Notably, even an ideal gas in a container breaks ergodicity in the above sense: the molecules in the container cannot visit the space outside the container. Obviously, this is due to the wall of the container inhibiting the molecules from escaping from the container. However, in reality, no containers are free from a gas leak. Any vacuum apparatus eventually loses its vacuum pressure if a vacuum pump is not operated. Microscopically, the potential barrier $E_b$ built in the metal wall impedes the diffusion of gas toward the outside. The finite value of an energy barrier makes the relaxation time $\tau$ of gas diffusion being finite. A rigid container is an idealized device to simplify physical problems by taking $\tau$ infinite. Even if the wall is removed, we find that perfect ergodicity does not exist. Air molecules cannot visit the space outside the atmosphere of the earth. The distribution of particles is continuously changed according to the gravitational potential $V(\mathbf{r})$. Ergodicity, as well as equilibrium, is subject to constraints.
2.3. Metastable, stable, and frozen states

In material science, it is often useful to distinguish metastable from stable states. The lowest-energy state means the stable state. However, in thermodynamics, the distinction is possible only in a relative sense. Diamond is by any means a stable equilibrium state. However, at room temperature, it is metastable compared with graphite, because the free energy of diamond is slightly higher than that of graphite. A mixture of hydrogen and nitrogen gases is very stable: no reaction occurs at room temperature. However, in an astrophysical timescale, they react to produce ammonia gas, as the difference in their energies shows. If a nuclear reaction is considered, all atoms except iron are metastable. There is no fundamental difference between stable and metastable equilibria. A metastable state \( j \) becomes the stable state in the scope of problem, whose timescale is shorter than the relaxation time \( \tau_j \).

Normally, defect states of a crystal are regarded as metastable states. Here we restrict the defects to intrinsic defects, such as vacancy and interstitial, with no foreign atoms. The ground-state energy of a defective crystal is higher than that of the perfect crystal. However, the defect structure remains unchanged unless it is annealed out at high temperatures. Consequently, it must be considered as an equilibrium state subject to the constraints imposed by the energy barriers around the defects.

**Corollary 1: Equilibrium states of a solid**

*If a solid does not change the current state in a time period \( \tau \), this state is an equilibrium state in that time period \( \tau \), regardless of whether the structure contains defects or not.*

By creating defects, many microscopic structures can be realized for a given crystal, and hence a crystal has as many numbers of equilibrium states as the numbers of atom arrangements that the crystal can have. Thanks to Corollary 1, we are free from asking whether quasicrystals are in equilibrium states or not.

![Figure 1](image-url)  
**Figure 1.** Distinction between metastable stable (a) and frozen state (b). (c) is the stable state.

This is particularly true for glasses. We do not need to bother with investigating which structure is the equilibrium state of a glass. Any glass currently existing is in an equilibrium state until its structure changes. A few remarks are mentioned regarding glasses. It is often claimed that the glass state is neither a stable nor metastable
state. The special notion frozen state is used to differentiate from the aforementioned metastable state. The frozen state is essentially a nonequilibrium state but is frozen by a strong viscous resistance. This conceptual distinction may be best seen in Fig. [1] it is taken from Wilks’s textbook ([4], p. 61). There seems no energy barrier in a frozen state. It is the classical resistance that impedes atom movements. However, if closely observed, we will find that the microscopic substance of viscous resistance is no more than energy barrier: frictional forces do not exist in the microscopic scale. Furthermore, a kinetically frozen state is used to emphasize the special property that the glass state is obtained by kinetically freezing from a supercooled liquid. However, the kinetic energy and potential energy are parts of the total energy, and can be incessantly interchanged ion the course of dynamics. The substance that freezes atom motions is the potential barrier, which is built in by the reduction of kinetic energy as the temperature decreases. Any kind of crystallization is a freezing process of the atoms of a liquid. The difference between glasses and crystals lies in the quantitative aspect that a glass has an overwhelming number of metastable states whose energies are close each other. Now, glasses can be obtained also by vapor deposition methods [13]. Since no supercooled liquid is mediated in this case, the word kinetically frozen liquid loses sense.

From Eq. (3), we observe that the equilibrium timescale is temperature dependent. As $T$ approaches 0, any value of energy barrier becomes infinitely large compared to the thermal energy $k_B T$. Hence, we conclude that

**Corollary 2: Equilibrium at $T = 0$**

All the existing solids retain their equilibrium states virtually in an infinite time, as temperature approaches 0, unless the environment alters.

At $T = 0$, the distinction between stable, metastable, and frozen states disappears. When considering the third law, it is often argued that metastable or nonequilibrium states cannot achieve a stable equilibrium state within a reasonable timescale at very low temperatures. However, in the present context, these states are already considered stable equilibrium states at low temperatures. At high temperatures, where transitions between different states occur within a relevant timescale, the distinction between metastable and stable states becomes meaningful.

3. Thermodynamic state space

3.1. Thermodynamic coordinates

3.1.1. General considerations  By defining equilibrium by Definition 1, we can define state variables without leading to the circular argument.

**Definition 3: Thermodynamic coordinate**

A thermodynamic coordinate is the time-averaged value of a dynamical variable under a constraint on the range in which the temporal value of the dynamical variable can vary.
In a mathematical form, a TC $X_j$ is written as

$$X_j = \frac{1}{t_0} \int_{\xi_j} X(t) dt, \quad (4)$$

where $t_0$ is the time period in which the average is taken. $t_0$ must be less than the relaxation time $\tau_j$, otherwise arbitrary. The notation $\xi_j$ in the integration denotes the constraint under which the dynamical variable $X(t)$ can vary. By defining a TC in this manner, it is understood that the time average of the corresponding variable $X(t)$ converges to a finite value $\bar{X}_j$, and that it does not depend on the period $t_0$. We refer to this property of a TC as definiteness. For example, for a gas in a box with volume $V$, the constraint is the wall of the box. The position, $x(t)$, of a gas molecule is constrained within the wall. In equilibrium, the molecule visits everywhere in the box with equal probability. The time average of the molecule’s position, $\bar{x}(t)$, is indeterminate. Thus, $x$ cannot be a TC. Next consider the spatial distribution function, $\delta(x', x(t))$, of a molecule at $x'$. The integration of this function over the inside of the box

$$X(t) = \int_V \delta(x', x(t)) dx', \quad (5)$$

gives the density-weighted volume. In equilibrium, the distribution is uniform in space and thus the time-averaged value $\bar{X}(t)$ gives the volume $V$. The time-averaged value $\bar{X}(t)$ thus becomes a TC $V$.

A constraint determines a TC. The constraint of a rigid wall $\xi_1$ of a cylinder specifies the volume $V$, which is a TC for the gas inside the cylinder when the gas is in equilibrium. If an additional wall $\xi_2$ is inserted inside the cylinder, we have two volumes, $V_1$ and $V_2$ as the TCs. In the same way, inserting an additional wall $\xi_n$ creates a new TC, $V_n$. In this manner, we find that there is a one-to-one correspondence between constraints and TCs. This relationship between a TC and a constraint is well described by Reiss ([57], Sec. I.8). This example shows that there is no fundamental restriction on the number of TCs. In the traditional tenet of thermodynamics, the thermodynamic properties of a macroscopic system are described by only a few TCs (for example [54]). However, in thermodynamics laws from the zeroth to the second law, there is no statement to restrict the number of TCs. Instead, the present argument shows the importance of the one-to-one correspondence between constraints and TCs.

Although any variable to meet Definition 2 can be a TC, imposing an additional requirement is desirable to retain consistency with the normal usage of state variable. The additional requirement for TC is distinguishability from other TCs. In the above example of the gas in a container, let us consider a dynamical variable $X_k(t) = \int_V \delta(x' - x_k(t)) dx'$ for an individual particle $k$. At equilibrium, the time average $\bar{X}_k(t)$ gives the same value $V$ for all the particles. There is no distinguishability among all the particles. They have redundancy. One TC is good enough to specify the gas state.

3.1.2. Thermodynamic coordinates of solids
For a gas, $V$ is only a TC for a fixed $T$. Any change in the shape of a container does not affect the properties of the gas, provided that $V$ is constant. On the other hand, any deformation of a solid causes a change in
the internal energy $U$, even for the same volume. This deformed solid is in equilibrium, provided that the deformation is supported by an external constraint. For the plastic deformation of a metal, dislocations are introduced, and $U$ is changed. The metal does not recover the original structure, even after the removal of the applied stress. The metal establishes a new equilibrium state with a different $U$. A displacement of even one atom in a solid (for example, by electron irradiation) changes its $U$. In all the above examples, once a solid establishes a new equilibrium state, each atom holds a new position $\vec{R}'_j$ as the equilibrium position, regardless of whether it is a regular position.

The equilibrium position $\vec{R}_j$ in a solid is the time average of the instantaneous position $\vec{R}_j(t) = \vec{R}_j + \vec{u}_j(t)$, where $\vec{u}_j(t)$ is the small displacement from the equilibrium position. Each atom has the definite value $\vec{R}_j$. Moreover, the equilibrium position $\vec{R}_j$ is distinguished from those of all the other atoms. Therefore, $\vec{R}_j$ meets the conditions of definiteness and distinguishability required for TCs.

**Corollary 3: Thermodynamic coordinates of a solid**

An equilibrium position of atom $\vec{R}_j$ is a thermodynamic coordinate for solids.

The number of atoms in a solid is quite large. However, it is still much smaller than the total number of microstates. Chemical species $\kappa$ at each position can be also a TC. There is no difficulty in treating this variable [48]. However, in the following arguments, we ignore this variable to avoid unnecessary complexity; therefore solids of only one chemical species are considered.

3.1.3. **Fundamental relation of equilibrium** In terms of the equilibrium state, the second law is expressed as follows.

**Postulation 1: The second law of thermodynamics**

*Among all the states of a system that have a given $U$ and are compatible with the given constraints, there exists one and only one stable equilibrium state.* [GB, p. 63]

In usual terms, this stable equilibrium state corresponds to the maximum entropy state. Under a given set of constraints, the state of a system is changed to establish the maximum of entropy.

Postulation 1 states that there is a one-to-one correspondence between equilibrium states and sets of constraints $\{\xi_j\}$. In Sec. 3.1.1, we have discussed that there is a one-to-one correspondence between $\{\xi_j\}$ and $\{X_j\}$. It follows that the equilibrium states of a system are completely and uniquely specified by the set $\{X_j\}$. Conversely, an equilibrium state fixes only one value $X_j$ for each $\xi_j$.

**Corollary 4: Existence of the fundamental relation of equilibrium**

*Under given constraints with a fixed $U$, the thermodynamic coordinates $\{X_j\}$ of a system are uniquely determined when the system is in equilibrium.*

The statement of one and only one equilibrium state in Postulation 1 implies the existence of a variable characterizing the equilibrium for each set of constraints. This variable is entropy $S$. Thus, there is a function that relates $S$ uniquely to all the other TCs,

$$S = S(U, X_1, \ldots, X_M).$$ (6)
This equation is called the fundamental relation of equilibrium (FRE) \[56\]. By changing the variables, other free energies take the same role. The most familiar one is the following energy expression \[54\],

\[
U = U(T, X_1, \ldots, X_M).
\]  

(7)

A special form of the FRE is useful for analyzing TCs. When the Hamiltonian of a system can be diagonalized with respect to \(\{X_j\}\), \(S\) is factorized as

\[
S = \sum_j S_j(X_j),
\]

(8)

where \(S_j(X_j)\) are the respective components. Although it is not necessary to assume this form in the following arguments, this elegant form is convenient to see how TCs contribute to the total entropy. In many cases, the factorized form likely holds at low temperatures, because energy barrier heights relative to the thermal energy become so high that all TCs are decoupled and become independent each other. It is known that the harmonic approximation holds at low temperatures, leading to

\[
S = k_B \sum_{k=1}^{M} \left[ (\bar{n}_k + 1) \ln(\bar{n}_k + 1) - \bar{n}_k \ln \bar{n}_k \right],
\]

(9)

where \(M = 3N_{at} - 3\). Here, \(\bar{n}_k\) is the Bose occupation number for the \(k\)-th phonon mode with the frequency \(\omega_k\). Equation (9) becomes 0 as \(T\) approaches 0.

The FRE has the following property \[49,54,56\].

**Corollary 5: Completeness of thermodynamic coordinates**

Any thermodynamic property of a system can be obtained from the fundamental relation of equilibrium.

If it were not complete, the above one-to-one correspondence would not hold.

Let us investigate the significance of the present Corollaries for solids. For solids, the set \(\{\bar{R}_j\}\) stands for the equilibrium structure of a given solid. By combining Corollaries 3, 4, and 5, we reach the trivial conclusion that all thermodynamic properties of a given solid are determined by the structure. From the view of solid state physics, this conclusion is taken for granted. However, by combining with Corollary 1, this has nontrivial consequence on thermodynamics \[48\]. Many properties of solids have history dependence: the mechanical properties of metals are affected by the previous thermal history; plastic deformations are the consequence of previous mechanical history; memory functions are the effects of previously applied fields. History-dependent properties are not uniquely determined by the current values of \(T\) and \(V\) only, so these properties were traditionally considered as nonequilibrium properties. Now, we have seen on rigorous grounds that \(\{\bar{R}_j\}\) are indeed the TCs. Any defect state, any static state that is a consequence of hysteresis is an equilibrium property as far as \(\{\bar{R}_j\}\) do not change within the time period \(\tau\) under consideration. If we obtain two glass samples with the same structure prepared using different methods, we cannot distinguish which sample was prepared by which method. This is precisely the meaning of state in the classical thermodynamics: a state is independent of the process by which the current state was obtained.
3.2. Thermodynamic state space

The number $M$ thermodynamic coordinates span the state space of $M$ dimensions. This space is called thermodynamic state space (word state space is already reserved in quantum mechanics).

**Definition 4: Thermodynamic state space**

The thermodynamic state space $\mathcal{A}$ spanned by $M$ thermodynamic coordinates, $\{X_j\}$, is expressed as

$$\mathcal{A} = (U, X_1, \ldots, X_M).$$

(10)

Here, for a convenience, the internal energy $U$ is counted as the 0th coordinate and is excluded from the dimension of the thermodynamic state space. As stated in Introduction, there is arbitrariness in the value $S$. This stems from the choice of TCs in a given problem. The value of entropy is thus dependent on the thermodynamic state space $\mathcal{A}$ on which $S$ is expressed:

$$S^\mathcal{A} = S(U, X_1, \ldots, X_M).$$

(11)

By expressing $S$ in a form Eq. (8), it is clear that $S^\mathcal{A}(A) \neq S^\mathcal{B}(A)$, when the entropy value of a state $A$ is evaluated in different spaces $\mathcal{A}$ and $\mathcal{B}$, although the two values refer to the same state.

**Corollary 6: Comparability condition**

To make it possible to compare entropy $S^\mathcal{A}(A)$ of state $A$ in thermodynamic state space $\mathcal{A}$ to entropy $S^\mathcal{B}(B)$ of state $B$ in thermodynamic state space $\mathcal{B}$, the two thermodynamic state spaces $\mathcal{A}$ and $\mathcal{B}$ must have the same dimensions.

It is always possible to find reversible paths in Eq. (1) when the two states ($A$ and $B$) are evaluated on the same space, because the state can be continuously changed from $A$ to $B$ without breaking constraints. The dependence of entropy on the space on which $S$ is expressed was pointed out by Grandy with different terminologies (45, p. 150). As is often the case in information theory, however, he ascribed the freedom in the entropy origin to our knowledge of TCs: if someone manipulates a new variable $X_{M+1}$ that we do not know, the entropy value will change. The entropy as a physical quantity should not be a subjective quantity. We are not free from choosing the entropy origin when the new variable $X_{M+1}$ is added. This is discussed in Sec. 3.3.

Let us consider the thermodynamic state space for solids. The thermodynamic state space is now expressed as

$$\mathcal{A} = (U, \{\bar{R}_j\})$$

(12)

with $3N_{\text{at}}$ dimensions. However, at temperatures sufficiently lower than the melting temperature, a different way of imposing constraints is needed for solids. This is because $\bar{R}_j$ is not a continuous variable but takes only discrete values, such as interstitial positions, in addition to the regular position. The state of the perfect crystal is presented by a single point $\{\bar{R}_j^1\}$ in the thermodynamic state space $\{\bar{R}_j\}$. Any disordered state of this crystal is also denoted by another point $\{\bar{R}_j^K\}$. We call this individual point (equilibrium) configuration.
Definition 5: Configuration

A configuration is specified by a set of equilibrium positions of atoms \( \{ \mathbf{R}_j \} \).

Configurations are separated from one another by energy barriers [63]. When there are \( N_c \) different configurations, the thermodynamic state space is expressed as:

\[
\mathscr{A} = (U, \{ \mathbf{R}^{(K)}_j \}),
\]

where \( (K) \) denotes the enumeration of all configurations \( K = 1, \ldots, N_c \) (\( N_c \): the number of different configurations). A configuration is specified by equilibrium atom positions \( \{ \mathbf{R}^K_j \} \); therefore, the configuration is akin to structure. At a fixed \( T \), different states of a solid mean different structures.

Since a configuration is defined by TCs \( \{ \mathbf{R}^K_j \} \), they have meaning only for solids. However, it may be useful to extend the concept of configuration to include liquids, as is done in Sec. 5. For liquids, an instantaneous configuration \( K(t) = \{ R_j(t) \} \) can be considered. When describing the transition from solid to liquid, we can employ \( K(t_m) \) at the time \( t_m \) of melting as the configuration of the liquid. In this manner, an analytic continuation is achieved. However, this extension is used only for this limited purpose.

3.3. Frozen and active coordinates

There is an interesting class of TCs. When Kline and Koenig studied the definition of a state variable, they considered the following example [64]. The properties of water in a container do not change when they are measured at any elevation \( H \) at which the container is held: they depend only on \( T \) and \( V \). The FRE is expressed by these two coordinates, \( (T, V) \equiv \{ X_j^0 \} \). However, there is the case that \( H \) affects the properties of water. In a hydraulic power plant, \( H \) is the most important coordinate. FRE depends on \( H \). When the gate of the upper pool is closed, the thermal communication between the top and bottom water is inhibited, and \( H \) does not enter the FRE. In this case, \( H \) is called a frozen coordinate.

Definition 6: Frozen coordinates

Frozen coordinates are the thermodynamic coordinates that are irrelevant to the present scope of the problem.

Let us denote frozen coordinate \( X \) by \( \hat{X} \). Then, the FRE is expressed as \( S(\{ X_j^0 \}; \hat{H}) = S_X(\{ X_j^0 \}) + S_H(\hat{H}) \). The part \( S_H(\hat{H}) \) is constant. The role of the constraint in this case is to completely inhibit \( \hat{H} \) from varying. When the gate is opened, the top water falls into the bottom pool, and \( H \) begins to vary and becomes a true variable. Now, we must take \( H \) into account in \( S \), as \( S = S(\{ X_j^0 \}, H) \). The gravitational potential of the top water is dissipated to the thermal energy of the bottom water. This is the process where the origin of entropy is reconstructed from one to another space. Because the constraint is broken, this process is an irreversible process.

The entropy of a perfect crystal is zero at \( T = 0 \). Despite this, a disorder due to the random distribution of isotopes lurks behind this perfection. This random distribution does not contribute to the thermodynamic properties of this crystal, and hence, the positions of isotopes are frozen coordinates. When an isotope enrichment
process is investigated, however, the distribution of isotopes becomes a real variable, and therefore must be considered. There are an infinite number of frozen coordinates \[44,46\]. The anthropomorphic feature of entropy originates from frozen coordinates. A frozen coordinate has no relevance to the current properties of the material. Therefore, a frozen coordinate has no \(T\) dependence in thermodynamic properties and is thus thermodynamically inactive.

**Definition 7: Active coordinates**
Non-frozen coordinates are active coordinates.

Any TC in Eq. \([7]\) is an active coordinate, because it affects other variables. In particular, an active coordinate brings \(T\) dependence to its thermodynamic properties through Eq. \([7]\). For solids, the active coordinate \(\mathbf{R}_j\) is associated with the phonon component \(\mathbf{u}_j(t)\) as \(\mathbf{R}_j(t) = \mathbf{R}_j + \mathbf{u}_j(t)\). This component introduces \(T\) dependence to \(S(\mathbf{R}_j)\) as in Eq. \([9]\), while frozen coordinates lack \(T\) dependence and remain unresponsive in thermodynamic reactions.

When a thermodynamic state space \(\mathcal{A} = (U, \{X_j\})\) of a material is a subspace of \(\mathcal{B} = (U, \{X_j\}, \{Y_j\})\) of the same material, we often need to compare the entropy \(S^\mathcal{A}(A)\) of state \(A\) in the space \(\mathcal{A}\) to the entropy \(S^\mathcal{B}(B)\) of state \(B\) in the space \(\mathcal{B}\). From Corollary 6, entropy comparison is justified only when two spaces have the same dimensions. This is established by patching the space \(\mathcal{A}\) with the frozen coordinates \(\{\hat{Y}_j\}\) as \((U, \{X_j\}; \{\hat{Y}_j\})\). In physics problems, the values \(\{\hat{Y}_j\}\) must always exist. This is because the subspace \(\{\{Y_j\}\}\) is a physical object, and therefore it must be possible to find state \(A\) in the subspace \(\{\{Y_j\}\}\): the previous value \(S^\mathcal{A}(A)\) is merely a consequence of ignoring the existence of \(\{\{Y_j\}\}\).

**Corollary 7: Extending thermodynamic state space**

It is possible to extend the thermodynamic state space \(\mathcal{A} = (U, \{X_j\})\) by adding frozen coordinates \(\{\hat{Y}_j\}\) to form \(\mathcal{B} = (U, \{X_j\}; \{Y_j\})\).

The entropy of \(A\) is transformed into

\[
S^\mathcal{B}(A) = S^\mathcal{A}(A) + S_0, \tag{14}
\]

where \(S_0 = S(\{\hat{Y}_j\})\) is a constant. Now, we can compare \(S^\mathcal{B}(A)\) with \(S^\mathcal{B}(B)\). The additive feature in Eq. \([14]\) is brought about by the property of frozen coordinates: the constraint on \(Y_j\) is so strong that the change in \(Y_j\) is completely decoupled to other TCs \(\{X_j\}\). When the constraint that fixes the value \(\hat{Y}_j\) of \(j\)th component is adiabatically removed, a spontaneous change is induced unless the initial state happens to be in equilibrium. The new equilibrium state \(A'\) has a different value \(Y_j'\) for this component. The adiabatic removal of a constraint is an irreversible process, so that an entropy production occurs by \(S_{\text{prod}} = S(Y_j') - S(\hat{Y}_j)\).

Let us consider the special property of frozen coordinates for solids. That the TCs are not continuous variables must be taken into consideration. The equilibrium position \(\mathbf{R}_j\) is a discrete variable. The equilibrium states of a solid are presented by any of the discrete points in the \(3N_{\text{at}}\) dimensional space \(\mathcal{A} = (U, \{\mathbf{R}_j^K\})\). Because any pair of two configurations is separated by the energy barrier, transitions between them
become inhibited as \( T \) decreases. At sufficiently low \( T \), a solid freezes at a certain configuration, say, \( K = 1 \). Only \( \{ \hat{R}_j \} \) are active coordinates: they have phonon contributions. Let us denote the thermodynamic state space spanned by the active coordinates as \( A = (U, \{ \hat{R}_j \}) \).

**Definition 8: Active configuration**

The active configuration comprises active coordinates \( \{ \hat{R}_j \} \) only.

The remaining configurations are frozen configurations. The full thermodynamic state space is expressed as

\[
\mathcal{B} = (U, \{ \hat{R}_j \}; \{ \hat{R}_j^{(K')} \}),
\]

(15)

where \( \{ \hat{R}_j^{(K')} \} = \{ \hat{R}_j^K \}_{K=2,...,N_c} \). We can compare the entropy of state \( A \) in \( A = (U, \{ \hat{R}_j \}) \) to the entropy of \( B \) in \( \mathcal{B} \) by patching frozen coordinates \( \{ \hat{R}_j^{(K')} \} \). Note that there is no idea of the “generic” active configuration for silicon. By Definition 7, each sample of silicon has a distinct active configuration of this sample: different samples have different defect structures. For this sample, the structures of all the other samples are frozen configurations. The specific heat of this sample is determined by the current structure but not by any of the other structures. Similarly, for a given sample of glass, the current structure of the sample is the active configuration, while all the other configurations are frozen configurations. The distinction between active and frozen coordinate is not made by our choice but is to be determined by experiment.

When the constraints that fix \( \{ \hat{R}_j^{(K')} \} \) are adiabatically removed, a spontaneous change is induced. Because the frozen coordinates have no phonon components, the contribution of \( \{ \hat{R}_j^{(K')} \} \) to entropy is the \( T \)-independent configurational entropy \( S_{\text{conf}} = k_B \ln N_c \), provided that all the configurations have the same energy. An entropy production occurs associated with the value \( S_{\text{prod}} = S_{\text{conf}} \).

### 3.4. Meaning of ensemble average

In statistical mechanics, there is a conceptual problem that has long been debated since Boltzmann provided a microscopic definition of entropy [46, 65, 66]. Owing to the probabilistic nature of entropy, the partition function \( Z \) must be evaluated by the ensemble average,

\[
Z = \sum_{K=1}^{N_c} Z_K,
\]

(16)

where \( Z_K \) is the partition function for the \( K \)-th configuration. Note that here ensembles are used to mean equilibrium configurations of solids, and hence \( Z_K \) is a function of \( \{ \hat{R}_j^K \} \). Hence, even summation of only one configuration, namely \( Z = Z_1 \), can present an equilibrium state of a solid. When calculating the entropy, the range of microscopic states that should be sampled must be determined. For glasses, the question is whether all configurations should be taken into account or not. There is no unique answer to this question. For the specific heat of diamond, only the perfect structure \( K = 1 \) is sufficient in calculating Eq. (16), even though there is no perfect crystal. However, if we
are interested in the concentration of vacancies, we need to take vacancy configurations $K \neq 1$ into account. If we investigate the phase transition between diamond and graphite at high pressures, we need to include the graphite structure in the members of $K$. In this way, the way of choosing ensembles hinges on the scope of a given problem. The important matter lies rather in how to compare the entropies of two equilibrium states. The comparison is possible only in the same thermodynamic state space. The classical definition of Eq. (1) stresses the comparability feature of entropy, while the summation in Eq. (16) is easy to hide this feature of entropy (Corollary 6).

4. The refinement of the third law expression

By establishing rigorous definitions of equilibrium and TC, we can construct the rigorous statement of the third law. All the existing structures of all solids are equilibrium states within their relaxation times (Corollary 1). They are specified by TCs $\{\tilde{R}_j\}$ (Corollary 3). Any one of them is the active coordinate unique to the given sample near $T = 0$ (Corollary 2 and Definition 8). Let us denote this active configuration as $K = 1$: thermodynamic state space is $\mathcal{A} = (U, \{\tilde{R}_j\})$. Thus, the full thermodynamic state space is expressed as $(U, \{\tilde{R}_j\}; \{\hat{R}_j^{(K')}\})$. The configuration $K = 1$ is only the equilibrium configuration near $T = 0$ within the constraints that specify $\{\tilde{R}_j\}$.

Postulation 2: The third law of thermodynamics

Entropy $S^\mathcal{A}$ of any configuration of a solid vanishes as $T$ approaches zero, provided that entropy is evaluated on the thermodynamic state space $\mathcal{A}$ that has only one active configuration, $\mathcal{A} = (U, \{\tilde{R}_j\})$.

Since all existing configurations become the active configuration near $T = 0$, the zero entropy holds for any configuration of any solid. In this manner, the third law attains the position as a universal law. The essential problem of the previous theories is that they did not acknowledge that a solid has many equilibrium states. The entropy in the third law refers to the entropy of each equilibrium state of a material among many equilibrium states that the material has. In the new theory, it is a meaningless question to ask what entropy of the generic silicon is, because different samples of silicon have different defects and thereby different entropy. Similarly, any sample of silica glass is in equilibrium, and the third law states that all samples of silica glass have zero entropy at $T = 0$.

When frozen coordinates are taken as TCs, the thermodynamic state space is extended to $\mathcal{B} = (U, \{\tilde{R}_j\}; \{\hat{R}_j^{(K')}\})$, and the entropy $S^\mathcal{B}$ has a finite value even at $T = 0$. The nonzero value is called residual entropy and is given by

$$S_{\text{res}} = S^\mathcal{B}(\{\hat{R}_j^{(K')}\}).$$

(17)

In the calorimetric method, the residual entropy $S_{\text{res}}$ is obtained in a cooling process from the liquid state at high temperatures. In the liquid state, all the configurations are observed in the measurement, meaning that the entropy is evaluated in the full space $\mathcal{B}$. Since the calorimetric measurement is expected to perform along a reversible
path according to Eq. (1), the thermodynamic state space does not change from $\mathcal{B}$ throughout the measurement. Because the calorimetric measurement gives only the difference in $S$, as 

$$\Delta S = S^\mathcal{B}(B) - S^\mathcal{B}(A) = \int_{T_a}^{T_b} C_p(T)d\ln T,$$

the constant value $S_{\text{res}}$ is not eliminated at $T = 0$. This is the reason for observing residual entropy. We should not compare a finite value $S^\mathcal{B} \neq 0$ to $S^\mathcal{A} = 0$.

A few remarks are mentioned on this new expression of the third law.

(i) The new expression is deduced from the present investigation about equilibrium that the current states of all the existing materials are equilibrium states, at $T = 0$. We do not need to wait until the structure achieves an ordered state, which is often claimed. At $T = 0$, the current state of glasses, random alloys, and defect states of solids all are already equilibrium states at present. The expression eliminates precarious expectations for future events to validate the third law.

(ii) No need arises to determine which state is the lowest state or to distinguish the metastable from the stable state. A conventional explanation for the residual entropy of disordered materials is that the lowest-energy state is an ordered state and accordingly the disordered states are not equilibrium states, which are out of subjects that the thermodynamics laws can apply. Now, this conventional explanation must be discarded. A fundamental difficulty of the conventional view that the order state is the lowest-energy state is that introducing this hypothesis makes it more fundamental than the third law is. Fundamental laws cannot be derived from other laws. Recent experimental results disprove this hypothesis. For boron crystal, the energy of the disordered structures is lower than that of the ordered structure [67]. Further examples for boron compounds are discovered [68,69].

(iii) The no-exception features (i) and (ii) have the third law being truly a universal law of physics. Hence, the expression is compatible with the universality of the unattainability of the absolute zero temperature. The logical equivalence of these two statements is proved in another paper [30].

5. Arguments on glass transition

The residual entropy of glass is always the source of confusions about the third law. Here, the recent arguments aroused by Kivelson and others [31,33] are discussed from the present view. In Sec. 4, we have seen that the entropy of a glass becomes zero at $T = 0$. This conclusion supports the argument of Kivelson and Reiss about the zero-entropy issue [31]. However, the present theory also admits the reality of residual entropy. How the two seemingly contradicting views are reconciled must be explained. Many confusions on the residual entropy of glass stem from this duality [32,37,40,41,43]. The real processes of the glass transition are irreversible due to atom relaxation, hysteresis,
and other side effects, which induce confusing arguments on the entropy evaluation \[70\]. Although the hysteresis affects residual entropy, the residual entropy remains even if the hysteresis is removed \[40\]. Hysteresis is not essential for the origin of residual entropy \[36, 71\], and hence, in the following, we ignore any effect caused by the hysteresis in order to concentrate on the principal mechanism of yielding residual entropy.

Let us consider a specific heat measurement of a glass on a heating process (\(a\)) from \(T = 0\) to \(T_m^+\), namely, slightly higher than the melting temperature \(T_m\). Here, specific heat is always inferred as isobaric specific heat \(C_p\), and hence, the subscript \(p\) is omitted in the following. During process (\(a\)), the glass substance undergoes transitions: (glass) \(\rightarrow\) (supercooled liquid) \(\rightarrow\) (normal liquid). Upon heating the glass, the specific heat \(C_g(T)\) of the glass increases. At the glass-transition temperature \(T_g\), the glass is transformed into the supercooled liquid exhibiting a jump \(\Delta C_g\) in the specific heat. The glass transition, however, has a finite width \(\Delta T_g = T_g^2 - T_g^1\): this region is called the transition region \[72\]. The finite width \(\Delta T_g\) breaks up the latent heat, which otherwise would appear. The specific heat in this region is denoted by \(C_{tr}\). Upon further heating, the supercooled liquid becomes the normal-state liquid at \(T_m\). The specific heat \(C_{sl}\) of supercooled liquid is generally larger than that of crystal \(C_c\): the difference is known as the excess specific heat \(C_{ex} = C_{sl} - C_c\).

Along heat path (\(a\)), the change in entropy from \(T = 0\) to \(T_m^+\) is obtained by integrating \(C\) as

\[
S_l(T_m^+) - S_g(0) = \int_0^{T_g^1} \frac{C_g(T)}{T}dT + \int_{T_g^1}^{T_g^2} \frac{C_{tr}(T)}{T}dT + \int_{T_g^2}^{T_m^+} \frac{C_{sl}(T)}{T}dT. (19)
\]

In the calorimetric method, the residual entropy \(S_g(0) \neq 0\) is determined by Eq. (19), provided that \(S_l(T_m^+)\) was obtained by an independent measurement. Since the calorimetric method is a well-established method for solids and liquids, the first and the last terms in the right-hand side of Eq. (19) are reliable. When Kivelson and Reiss claimed that there is no residual entropy for glass, the only conceivable explanation for the contradiction with experimental residual entropy is that the measurement of the second term in the right-hand side Eq. (19) is wrong \[31\]. They attributed this error to the irreversibility of the glass transition process. However, as already studied by others \[36, 41, 71\], the effect of irreversibility of the glass transition process can be suppressed at minimum by careful measurement. Even if the irreversibility is removed, there must be an issue in evaluating the second term in Eq. (19).

According to Postulation 2, the conclusion \(S_g(0) = 0\) is derived by using \(\mathcal{A} = (U, \{\bar{R}_j\})\) as the thermodynamic state space when evaluating \(S\), where \(K = 1\) denotes an active configuration. The situation of the thermodynamic state space is shown in Fig. 2 (a). Here, the thermodynamic state space of liquid is partitioned by configurations \(K\). But readers should remember that this is done only because of the limited utility, as explained at the end of Sec. 3.2. We measure specific heat along the line \(K = 1\) until reaching at \(T_g\). On the other hand, the measurement of \(S_l\) assumes the use of the thermodynamic state space \(\mathcal{B} = (U, \{\bar{R}_j^{(K)}\})\) of all configurations because all the atoms randomly move throughout the liquid. Consequently, the thermodynamic state space
must be changed from $\mathcal{A}$ to $\mathcal{B}$ at $T_g$,

$$(U, \{\hat{\mathbf{R}}_j^{\mathcal{K}}\}; \{\hat{\mathbf{R}}_j^{\mathcal{K'}}\}) \rightarrow (U, \{\hat{\mathbf{R}}_j^{\mathcal{K}}\}).$$

This indicates that the frozen coordinates $\{\hat{\mathbf{R}}_j^{\mathcal{K'}}\}$ are fully activated on heating: the corresponding constraints $\xi(\{\hat{\mathbf{R}}_j^{\mathcal{K'}}\})$ have been removed. Removing constraints is an irreversible process, and accordingly, an entropy production $S_{\text{prod}}$ occurs without heat exchange: an uncompensated entropy increase occurs. This is similar to the entropy increase during the free expansion of gas: a gas initially in one side of a container that is separated by an internal wall is expanded by quickly removing the wall. In fact, the glass transition viewed from the low temperature side can be looked upon as a free expansion of the space that atoms can occupy. This uncompensated entropy increase corresponds to the configuration entropy $S_{\text{conf}}$, which turns into the residual entropy $S_{\text{res}}$.

$$S_{\text{res}} = S_{\text{conf}} = S(\{\hat{\mathbf{R}}_j^{\mathcal{K'}}\}).$$

Therefore, the entropy increase by $S_{\text{res}}$ is missing in the calorimetric method. This argument, however, does not mean that the calorimetric measurement in the transition region is wrong. The physics does not change. The problem lies on our side: we changed the entropy origin associated with the change in the thermodynamic state space from $\mathcal{B}$ to $\mathcal{A}$.

In contrast, in a cooling process, we see a different situation. Let us consider a cooling process (b) from liquid state: (normal liquid) $\rightarrow$ (supercooled liquid) $\rightarrow$
In this case, the initial entropy is evaluated in the thermodynamic state space \( \mathcal{B} = (U, \{ R_j^K \}) \). Hence, \( S_B^\emptyset(T_m+) \) retains the component of configuration \( S_{\text{conf}} \). Upon cooling down to \( T = 0 \), \( S_g^\emptyset(0) \) is obtained by subtracting the right-hand side of Eq. (19) from \( S_B^\emptyset(T_m+) \). This subtraction does not eliminate the component \( S_{\text{conf}} \), and this nonzero component remains at \( T = 0 \), which is observed as the residual entropy. Throughout the entire cooling path \((b)\), the same thermodynamic state space \( \mathcal{B} \) is used, and hence, the cooling process is reversible. Thus, observing the residual entropy in a cooling process is in accordance with the thermodynamics principles. The conceptual difficulty of this measurement is that even though an obtained sample of glass fixes its structure at a particular configuration, \( K = 1 \), nonzero residual entropy implies that the entropy of this sample is influenced by the other configurations. How does this sample know other structures? This problem of causality was the original question aroused by Kivelson and Reiss [31].

Figure 2 (b) illustrates how this confusing problem occurs. Consider the entropy value of this glass at temperature \( T_1 \) little lower than \( T_g \). Upon cooling from the liquid, the structure of glass is fixed at a certain configuration, namely, \( K_1 \). Neglecting all the other configurations \( K' \neq K_1 \) must cause a decrease in \( S \). This decrease must be compensated by an increase in \( S \) somewhere: otherwise, the second law would be violated [73]. Sometimes this problem is explained that, although \( K_1 \) is fixed, we do not know which one is realized among many configurations [7]. This explanation is partly correct, but it sounds something subjective, which provokes a further question (p. 86): if we were to know the structure of this sample exactly, would \( S_{\text{res}} \) become zero? Entropy in physics must be independent of our knowledge [75–77]. The residual entropy is a property of material. When entropies of two states are compared, this must be done along a reversible path connecting the two states, as Eq. (1). The state having nonzero \( S_{\text{res}} \) at low temperature thus should be connected to a high-temperature state by a reversible path. This reversible path can be obtained by a process of going back and forth between the two temperatures. After reaching \( K_1 \) at \( T_1 \), the sample is reheated to \( T_g+ \). Then, a different configuration \( K_2 \) of the glass is obtained by cooling from \( T_g+ \). We can repeat this process by any number \( m \) of times as we like, reaching a different configuration \( K_m \). At a sufficiently large \( m \) times, we can explore the entire space \((K)\). Only in this limit, a reversible process is achieved, because, by definition, missing some part of \((K)\) cannot be reversible. By lowering \( T_1 \) in this process, we can, in principle, sample all the configurations and achieve a reversible path even very low temperatures, and thus nonzero value \( S_{\text{res}} \) is obtained.

However, note that, in the repeated cooling-heating process, the caloric measurement explores only one configuration \( K_i \) during one step of cooling or heating between \( T_g+ \) and \( T_1 \). By constraining the structural change in this subspace \( K_i \) only, one-step process becomes reversible. The entropy change \( \Delta S_i = S_g(T_1) - S_l(T_g+) \) in one cooling step is thus given by the change in entropy in the subspace \( K_i \), namely, \( \Delta S_i = \Delta S_i^{K_i} = S_g^{K_i}(T_1) - S_l^{K_i}(T_g+) \). The remaining part \( S_{\text{res}} \) is included in the integration constant. For any final configuration \( K_i \), the calorimetric measurement gives
the same value $\Delta S_i$ with the same integration constant. This is a property of a glass, but is not the consequence that the glass experienced the all possible configurations.

Finally, we show that our conclusion $S_{res} = 0$ can be obtained even in the cooling process. This process is the reversed process of $(a)$ and is designated as $(\bar{a})$. In process $(\bar{a})$, the configuration entropy must vanish by cooling across $T_g$. This means that the thermodynamic state space changed from \( \mathcal{B} \) to \( \mathcal{A} \) at $T_g$. Mauro and Gupta viewed this process as a spontaneous entropy decrease because of the lack of latent heat \[33\] \[35\]. The uncompensated decrease of entropy conflicts with the second law. Mauro and Gupta explained this fundamental difficulty as an intervention of external constraint: the constraint in this case is, in their interpretation, the finite time of observation by human. This view again sounds something subjective, seeking the solution outside physics. The real solution lies in how to find a reversible path to connect the zero-entropy state from the liquid state. As seen above, process $(a)$ is an irreversible process. It is impossible to invert an irreversible process without leaving any effect on the environment. However, it is possible at the expense of external work. Reducing the thermodynamic state space from \( \mathcal{B} \) to \( \mathcal{A} \) can be achieved by a mechanical compression. For example, first, the liquid state at near $T_g$ is isothermally compressed. Because $T_g$ increases with increasing pressure $P$, at a sufficiently high pressure $P_1$, the liquid is condensed to the solid state: we suppose this solid state as the glass state. In this process, the TCs were changed from \( \{\bar{R}_j^{(K)}(T = T_g, P = 0)\} \) to \( \{\bar{R}_j^{K_1}(T = T_g, P = P_1)\} \) in a reversible manner. At this point, the configuration component $S_{conf}$ has been removed. Next, this glass is cooled down to $T = 0$, maintaining $P = P_1$. Finally, the glass is decompressed to restore the glass state \( \{\bar{R}_j^{K_1}(T = 0, P = 0)\} \) at ambient pressure. Although the heat path is different from the original cooling path, it is our leaning from elemental thermodynamics that the path in Eq. (1) is not necessarily a real path that the final state $B$ was obtained. In the reversible path, the cost for the entropy decrease is paid by the work to compress. The increase in $U$ of glass is partly dissipated through heat rejection to the environment. Hence, the total entropy does not decrease. This is similar to isothermal and quasi-static compression of a gas by a piston in a cylinder: the decrease in entropy is compensated by heat rejection to the environment from the internal energy of the gas, which increased due to the applied work. Some ideas connecting disordered states to the ordered state are discussed in \[78\] \[79\].

6. Conclusion

We have established the unambiguous statement of the third law using Postulation 2. This does not leave exceptions, including glass. It is independent of whether the state is the lowest-energy state or not, and is also independent of whether the state is in equilibrium or not in the traditional sense. To reach this conclusion, the definition of equilibrium was revisited. Equilibrium is defined only under a certain set of constraints \( \{\xi_j\} \), which restricts the timescale in which the equilibrium maintains. Each constraint specifies a thermodynamic coordinate $X_j$, and the set \( \{X_j\} \) defines the thermodynamic
state space $\mathcal{A}$. The entropy value is uniquely determined only on specifying the thermodynamic state space, as $S^{eq}$. From this foundation, it is deduced that the TCs of solids are the time-averaged positions of atoms $\bar{R}_j$. The set $\{\bar{R}_j\}$ determines the equilibrium configuration of a solid. When temperature approaches to zero, only one configuration $\{\bar{R}_j^{(K=1)}\}$ is thermally activated, which is only the equilibrium state at $T = 0$ within the given constraints. The third law of the zero entropy is stated on the space of this equilibrium configuration. Residual entropy arises when the entropy is evaluated on an extended space including frozen coordinates $\{\hat{R}_j^{(K')}\}$, which were active at high-temperature measurements. How to connect these two spaces has been explained by taking the glass transition as an example. Many confusing problems of the entropy of glass stem from overlooking reversible paths in the definition of entropy difference. Reversible paths can be found only within the same thermodynamic state space, unless external factors intervene.

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References

[1] Fowler R and Guggenheim E A 1952 *Statistical Thermodynamics* 3rd ed (London: Cambridge)
[2] Wilson A H 1957 *Thermodynamics and Statistical Thermodynamics* (Cambridge: Cambridge)
[3] Lewis G N and Randall M 1961 *Thermodynamics, revised by K. S. Pitzer and L. Brewer* 2nd ed (New York: McGraw-Hill)
[4] Wilks J 1961 *The Third Law of Thermodynamics* (London: Oxford)
[5] Guggenheim E A 1967 *Thermodynamics and Advanced Treatment for Chemists and Physicists* 5th ed (Amsterdam: North-Holland)
[6] Beattie J A and Oppenheim I 1979 *Principles of Thermodynamics* (Amsterdam: Elsevier)
[7] Eastman E D and Milner R T 1933 *J. Chem. Phys.* 1 444
[8] Gutzow I and Schmelzer J W P 2009 *J. Non-Cryst. Solids* 355 581
[9] Simon F E 1930 *Ergebn. exak. Naturwiss* 9 222–274
[10] Simon F E 1951 *Zeit. f. Naturforsch.* 6a 397
[11] Today, this view for thermodynamics is seriously subjected to criticism. The first law says the energy conservation, which holds irrespective of whether the state is equilibrium or not. The second law says impossibility of the perpetual-motion of engine of the second kind, how the engine utilizes nonequilibrium states.
[12] Even a recent study on the third law adapted this traditional view for residual entropy [29].
[13] Berthier L and Ediger M D 2016 *Phys. Today* 69 (1) 40
[14] Zhao J, Simon S L and McKenna G B 2013 *Nat. Commun.* 4 1783
[15] Landsberg P T 1957 *Rev. Mod. Phys.* 28 363
[16] Landsberg P T 1978 *Thermodynamics and Statistical Mechanics* (Oxford: Oxford)
Third law expression

[17] Landsberg P T 1997 Am. J. Phys. 65 269
[18] Buchdahl H A 1966 The Concepts of Classical Thermodynamics (Cambridge: Cambridge)
[19] Hasse R 1971 Physical Chemistry: An Advanced Treatise vol 1/ Thermodynamics ed Jost W (New York: Academic)
[20] Tolman R C 1979 The Principles of Statistical Mechanics (New York: Dover Pub.)
[21] Tisza L 1966 Generalized Thermodynamics (Cambridge: MIT Press)
[22] Assael M J, Goodwin A R H, Stamatoudis M, Wakeham W A and Will S 2011 Commonly Asked Questions in Thermodynamics (Boca Ranton: CRC Press)
[23] Bailerlein R 1999 Thermal Physics (Cambridge: Cambridge)
[24] Waldram J R 1985 The Theory of Thermodynamics (New York: Cambridge)
[25] K. Shirai, cond-mat.stat-mech/1804.02122
[26] Hatsopoulos G N and Keenan J H 1965 Principles of General Thermodynamics (New York: John Wiley & Sons, Inc.)
[27] Levine I N 1983 Physical Chemistry 2nd ed (New York: McGraw-Hill)
[28] McNabb-III J R, Fujita S and Suzuki A 2017 J. Mod. Phys. 8 839
[29] Masanes L and Oppenheim J 2017 Nature Commun. 8 14538
[30] K. Shirai, cond-mat.stat-mech/1804.01672
[31] Kivelson D and Reiss H 1999 J. Phys. Chem. B 103 8337
[32] Speedy R J 1999 J. Phys. Chem. B 103 4060
[33] Mauro J C, Gupta P K and Loucks R J 2007 J. Phys. Chem. 126 184511
[34] Gupta P K and Mauro J C 2007 J. Chem. Phys. 126 224505
[35] Gupta P K and Mauro J C 2008 J. Chem. Phys. 127 067101
[36] Goldstein M 2008 J. Chem. Phys. 128 154510
[37] Reiss H 2009 J. Non-Cryst. Solids 355 617
[38] Goldstein M 2011 J. Non-Cryst. Solids 357 463
[39] Takada A, Conradt R and Richet P 2013 J. Non-Cryst. Solids 365 53
[40] Möller J, Gutzow I and Schmelzer J W P 2006 J. Chem. Phys. 125 094505
[41] Aji D P B and Johari G P 2010 J. Phys. Chem. B 114 9578
[42] See also a special volume of Entropy 20 (2018); especially, J. W. P. Schmelzer and T. V. Tropin, p. 103; S. P. Gujrati, p. 149; S. V. Nemilov, p. 187; A. Takada, R. Conradt, and P. Richet, p. 218
[43] Gupta P K and Mauro J C 2009 J. Chem. Phys. 130 094503
[44] Grad H 1961 Commun. Pure Appl. Math. 14 323
[45] Grandy-Jr W T 2008 Entropy and the Time Evolution of Macroscopic Systems (Oxford: Oxford)
[46] Jaynes E T 1965 Am. J. Phys. 33 391
[47] Zemansky M and Dittman R 1997 Heat and Thermodynamics 7th ed (New York: McGraw-Hill)
[48] K. Shirai, cond-mat.stat-mech/1812.08977
[49] Gyftopoulos E P and Beretta G P 2005 Thermodynamics - Foundations and Applications (New York: Dover Pub.)
[50] Shirai K 2020 J. Phys. Commun. 4 085015
[51] Shirai K 2021 J. Phys. Commun. 5 015004
[52] Shirai K 2021 J. Phys. Commun. 5 095013
[53] Shirai K, Watanabe K and Momida H 2022 J. Phys.: Condens. Matter 34 375002
[54] Callen H 1985 Thermodynamics and an Introduction to Thermostatistics 2nd ed (New York: Wiley)
[55] Beauragard and Tribus wrote: “There is no way out of the dilemma that equilibrium is defined via thermodynamic constructs which constructs were in turn defined for the equilibrium state” [80].
[56] Gibbs J W 1906 Scientific Papers vol I: Thermodynamics (New York: Longmans, Green and Co.)
[57] Reiss H 1996 Methods of Thermodynamics (New York: Dover Pub.)
[58] Corti D S, Debenedetti P G, Sastry S and Stillinger F H 1997 Phys. Rev. E 55 5522
[59] Ponga E A, Rodriguez-Tinoco C, Cerullo G, Ferrante C, Rogriguez-Viejo J and Scopigno T 2015 Proc. Natl. Acad. Sci. 112 2331
[60] Brüning R and Samwer K 1992 Phys. Rev. B 46 11318
Third law expression

[61] Hecksher T, Nielsen A I, Olsen N B and Dyre J C 2008 Nature Phys. 4 737
[62] Penrose O 1979 Rep. Prog. Phys. 42 1937
[63] In the literature, the term configuration is sometimes used for gases and liquids too. Instantaneous positions \( \{ R_j(t) \} \) are regarded as configuration. However, here we restrict the term only when atom positions have the definite average values.
[64] Kline J and Koenig F O 1957 J. Appl. Mech. 103 29
[65] Lebowitz J L 1993 Phys. Today 46 (9) 32
[66] Uffink J 2001 Stud. Hist. Phil. Mod. Phys. 32 305
[67] Ogitsu T, Gygi F, Reed J, Motome Y, Schwegler E and Galli G 2009 J. Am. Chem. Soc. 131 1903
[68] Xie K Y, An Q, Toksoy M F, McCauley J W, Haber R A, Goddard-III W A and Hemker K J 2015 Phys. Rev. Lett. 115 175501
[69] Rasim K, Ramlau R, Leithe-Jasper A, Mori T, Burkhardt U, Borrmann H, Schnelle W, Carbogno C, Scheffler M and Grin Y 2018 Angew. Chem. Int. Ed. 57 6130
[70] Langer S A and Sethna J 1988 Phys. Rev. Lett. 61 570
[71] Bestul A B and Chang S S 1965 J. Chem. Phys. 43 4532
[72] Moynihan C T, Easteal A J, Wilder J and Tucker J 1974 J. Phys. Chem. 78 2673
[73] Cooling causes an increase in the entropy of the environment. But this was already compensated by the decrease in \( \int C_d \ln T \) of glass. Further decrease in \( S \) occurs, which is the issue to be answered.
[74] Sethna J P 2017 Statistical Mechanics: Entropy, Order Parameters, and Complexity (Oxford: Clarendon Press)
[75] Leff H S and Rex A F (eds) 2003 Maxwell’s Demon 2: Entropy, Classical and Quantum information, Computing (Bristol: IOP Pub.)
[76] Jaynes E T 1979 The Maximum Entropy Formalism (Cambridge, Massachusetts: MIT Press)
[77] Denbigh K G 1981 Chem. Brit. 17 168
[78] Suga H 2005 Proc. Jpn. Acad., Ser. B 81 349
[79] Kozlinski E and Lambert F L 2008 Entropy 10 274
[80] d Beauragard O C and Tribus M 2003 - Maxwell’s Demon 2: Entropy, Classical and Quantum information, Computing ed Leff H S and Rex A F (Bristol: IOP Pub.)