A thermodynamic description of the glass state and the glass transition

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Abstract
Many properties of solids, such as the glass state, hysteresis, and memory effects, are commonly treated as nonequilibrium phenomena, which involve numerous conceptual difficulties. However, few studies have addressed the problem of understanding equilibrium itself. Equilibrium is often assessed based on the assumption that its thermodynamic state should be solely determined using temperature and pressure. However, this assumption must be fundamentally reappraised from the beginning because no rigorous proof for this assumption exists. Previous work showed that for solids, the time-averaged positions of all constituent atoms of the solid are thermodynamic coordinates (TCs). In this study, this conclusion is further elaborated starting from the principles of solid-state physics. This theory is applied to glass materials, for which many challenges remain. Results show that first, the glass state, which is the state after freezing, is an equilibrium state under given constraints. Accordingly, the properties of a glass can be solely described using the present time-averaged atom positions, irrespective of their history, which is consistent with the definition of a state in the thermodynamic context. Any quantity that is determined using TCs can be used as an order parameter. Second, although the traditional view that the transition state during the glass transition is a nonequilibrium state is correct, whether it reaches the supercooled-liquid state given sufficient time is highly questionable. The final state must be an inhomogeneous mixture of solid and liquid phases. In the liquid phase, the atom positions are missing from the set of TCs. The degeneration of the state space occurs, which corresponds to an increase in configuration entropy. Conversely, when the phonon and structural parts of the atom positions are well separated, the time-averaged atom positions in the solid part remain as TCs. In this manner, the transition state can be described using a reduced set of TCs as a function of time. An important outcome of this theory is that the hysteresis of the glass transition can be described using the present values of TCs through the structural-dependent energy barrier. Complicated response functions describing the history, which are widely used in glass literature, are unnecessary. The expense of this simplification is that, in a rigorous sense, all the atom positions are needed for TCs. However, in most cases, only a few TCs are sufficient to describe the transition state, if these TCs are suitably chosen.

1. Introduction

1.1. Background
Thermodynamics is an elemental discipline underpinning the developments of a wide range of scientific and engineering fields. The principles of thermodynamics are robust and are not invalidated by the advent of quantum mechanics. Despite this universal characteristic, severe restrictions are imposed on applying thermodynamics to investigate the properties of solids. Many problems arise from the conceptual difficulty of defining state variables. This is easy to answer in an introductory course on thermodynamics, which teaches us
that for gases, equilibrium states are described solely by two state variables: temperature $T$ and pressure $p$. Many researchers believe that the same holds true for solids. Here, we restrict ourselves to the solids of one chemical component only. Moreover, electronic and magnetic properties are ignored. As later discussed, many phenomena in solids cannot be described solely using the two variables $T$ and $p$. For example, the physical properties of plastics cannot be described solely using $T$ and $p$, and the mechanical properties of metals vary depending on heat treatments. These difficulties have been averted by considering these phenomena to be nonequilibrium and no longer treating them within the framework of thermodynamics. However, all solids exhibit hysteresis to a certain degree. If thermodynamics were unable to explain such commonly observed phenomena, it would risk being relegated from the top ranks of physics principles.

Bridgman was the first to confront the hysteresis issue from the thermodynamics viewpoint when he stated: ‘But the admission of general impotence in the presence of irreversible processes appears on reflection to be a surprising thing. Physics does not usually adopt such an attitude of defeatism’ ([1], p.133). The present author advocates Bridgman’s viewpoint. His approach to describing plastic deformation is remarkable [2]; he treats stress and strain as independent variables—in elastic theory these are interrelated with each other. Unfortunately, Bridgman’s theory has not been further developed.

No rigorous proof is available that $T$ and $p$ are the only independent state variables for solids. However, despite this lack of proof, this proposition is decisive when deciding whether a property is an equilibrium property. In view of the importance of this proposition in a wide range of applications, it must be critically examined. To this end, we must first define equilibrium; however, this requires understanding what state variables are. Thus, the argument becomes circular, which makes a coherent definition of equilibrium difficult to obtain [3]. This logical difficulty was resolved by Gyftopoulos and Beretta, who provided a coherent framework of thermodynamics [4]. The basis of their theory relies on the fact that numerous equilibrium states exist for a given system, whereas one and only one stable equilibrium state exists for a given set of constraints. The latter part of the preceding sentence is an alternative expression of the second law of thermodynamics. Every equilibrium state is classified by constraints. Thus, a full set of constraints is required to specify an equilibrium state.

Previous work examined the consequences of applying this theory of equilibrium to solids [5]. Hereinafter, the term ‘thermodynamic coordinates’ (TCs) is used for state variables, following Zemanski [6]. The result is that the time-averaged positions of all atoms comprising a solid are necessary and sufficient TCs for the solid. At first glance, this conclusion seems strange, because too many TCs are needed for a thermodynamic description, which seems to be in conflict with the spirit of thermodynamics (i.e., describing many-particle systems with a minimum of variables) [7]. However, the most important characteristics of a TC are definiteness and distinguishability, which are explained below.

As opposed to a gas, a solid can exist in a variety of equilibrium states. For example, displacement of a single atom in a solid to an interstitial site creates another state of the solid, which is an equilibrium state because the defect structure does not vary unless it is annealed out. The thermodynamic properties of the state thus created differ from those of a perfect crystal because the displacement modifies the phonon spectrum, which in turn alters the specific heat of the crystal. In fact, an overwhelming number of atom displacements are possible, each of which corresponds to a distinct equilibrium state. The definiteness mentioned above implies that a unique value of TC can be attached to each equilibrium state. For a gas in equilibrium, there is no unique position for each atom. Only volume $V$ has a unique value, provided $T$ is fixed. Conversely, the atoms in a solid have definite average positions, that is, equilibrium positions, implying that the time-averaged positions of atoms characterize the equilibrium states of the solid. Distinguishability means that every atom can be distinguished based on its equilibrium position from all other atoms. For a gas, all atoms share the same volume and distinguishability is lost upon time averaging.

The fact that a large number of atom positions exist does not conflict with the principles of thermodynamics. In the first law of thermodynamics,

$$dU = TdS - \sum_{j=1}^{M} F_j \cdot X_j,$$  \hspace{1cm} (1)

nothing restricts the number $M$ of state variables $\{X_j\}$. Here, $U$ is internal energy, $S$ is entropy, and $F_j$ is the generalized force corresponding to $X_j$. The microscopic nature of atom positions is irrelevant for being a TC; the word ‘microscopic’ only makes sense when viewed from the human scale. The universal laws of physics must hold independent of our scale. The above definitions of equilibrium and TCs are not a matter of interpretation. They are logical and rigorous consequences of the second law of thermodynamics ([4], p. 119).

1.2. Purpose of this paper
This study applies this definition of equilibrium to the glass problem, which is one of the most interesting applications of the theory. In the early days, glass confronted physicists with a serious difficulty because it seemed to contradict the third law of thermodynamics. Glasses have nonzero entropy even when approaching $T = 0$. 


Simon and contemporaries explained this contradiction by deeming the glass state to be a nonequilibrium state \[8, 9\]. Since then, numerous studies over the past century used this explanation \[10–17\]. However, conceptual problems remain unsolved: the nature of the order parameter in glasses, the Kauzmann paradox \[18\], and the Prigogin–Defay relation are still being debated. All these issues are deeply related to thermodynamic equilibrium.

To address these issues, the present work describes the glass state from a novel view of thermodynamics. Briefly speaking, all static states are equilibrium states, leading to the conclusion that glass is in equilibrium state once solidification is completed, which significantly differs from the widely held view that glass is in a nonequilibrium state. Next, a thermodynamic description of the glass transition is provided, focusing on the specific heat \( C \) versus \( T \) (in the main text, \( C \) refers to the isobaric specific heat and the subscript \( p \) is omitted). Glass transitions are nonequilibrium phenomena, because, by definition, transitions are time dependent. Despite this, thermodynamics proves quite useful for analyzing processes. A significant advantage of the present theory is that, under appropriate conditions (which we later call the adiabatic approximation of the second kind), the transitions can be described based only on the present state, so complicated functions of past history are not required. An important outcome of this approach is that the activation energy of the glass transition is a strong function of enthalpy and therefore of temperature. This provides useful insights for studying many solid-state phenomena that are presently considered as nonequilibrium phenomena, such as the memory function of phase-change materials \[19\] and the aging and rejuvenating effect of spin glasses \[20\].

This paper is organized as follows: section 2 summarizes the general framework of thermodynamics based on a unambiguous definition of equilibrium, which connects the work of \[5\] with the present discussion. In addition, section 2 provides a microscopic derivation of the TCs of solids and the hierarchy of approximations for thermodynamic descriptions. Section 3 describes the glass state. A major difference with the conventional view held by most who study glasses is that, once solidified, glasses are indeed in equilibrium. Section 4 concludes the study. Because this study covers a wide range of research fields, some notions might be unfamiliar to readers outside the specific field. Supplementary material collects those questions commonly asked available online at stacks.iop.org/JPCO/4/085015/mmedia.

2. Grand work on the thermodynamics of solids

2.1. Thermodynamic equilibrium

2.1.1. Equilibrium and thermodynamic coordinates

We begin by defining equilibrium. Although no essential differences should exist in the thermodynamics principles between gases and solids, an unambiguous definition of equilibrium is required for solids because of the variety of equilibria possible in solids and the many difficulties that arise therefrom. The existence of numerous equilibria combined with the second law of thermodynamics clouds the picture of stable equilibrium, making it difficult to understand ((4), p.63). For a gas, the shape of the container in which the gas is enclosed is irrelevant to the thermodynamic properties of the gas, provided the volume is the same. Therefore, the shape is not a TC. In contrast, a solid can be deformed in various ways and all deformations alter the internal energy of the solid. Hence, the work part of equation (1) is expressed by \(- V \int \sigma (r) d\varepsilon (r)\), where \(\sigma \) and \(\varepsilon\) are the stress and strain, respectively. The strain at each point in the solid is regarded as a TC. This implies that the number of the TCs, \( M \) in equation (1), is virtually infinite.

It is nonsensical to speak of equilibrium without specifying constraints. Gibbs noticed this role of constraints—passive resistance in his words—more than one century ago \[21\], and equilibrium holds only within the given constraints. However, at the time, the nature of constraints was unknown. Today, we can answer this question: constraints are no more than energy barriers of any kind. Another problem that has not been sufficiently addressed is the relationship between constraints and TCs. Reiss may have been the first to realize that a one-to-one correspondence exists between a constraint \(\xi\) and a TC \(X_j\) \[22\]. A constraint specifies the range of a quantity \( x \) (i.e., the position, energy, chemical species, or any other observable) that the particles can visit. At a finite \( T \), the quantity \( x(t) \) accompanies fluctuations within the constraint as a function of time \( t \). A time-averaged value of \( x(t) \) over a period \( t_0 \),

\[
X_j = \frac{1}{t_0} \int_0^{t_0} x_j(t) dt,
\]

is fixed in an equilibrium state. In this manner, a constraint creates a TC.

The remaining problem is how to define equilibrium without using TC as a predefined quantity. This problem was resolved by Gyftopoulos and Beretta \[4\], who defined equilibrium as follows:
**Definition 1 (Thermodynamic equilibrium).** It is impossible to change the stable equilibrium state of a system to any other state with the sole effect on the environment being a raise of the weight.

In short, the raise of the weight means performing positive work on the environment. This manner of defining equilibrium does not require knowledge about the details of the internal structure of the system in question. We can treat the interior of the system as a black box; knowledge of how the system affects the environment is the sole requirement. This definition of equilibrium is consistent with an intuitive understanding of equilibrium: only static states are equilibrium states. Numerous equilibrium states exist for a given system. By combing definition 1 to the expression of the second law that one and only one stable equilibrium state exists for a given set of constraints [4], we find that a system is characterized by a full set of constraints. Constraints thus include everything to determine the structures of a material.

If one constraint is altered, the equilibrium state changes. The properties of a solid change when the atom configuration changes. Displacing one atom changes the properties of the solid, which is exploited for memory and switching devices in electronics. A phase transition that involves displacement produces different properties of a solid; for example, ferroelectric materials have different polarizations depending on the applied electric field. A collective displacement of atoms creates dislocations, which produce different mechanical properties. These defect states are in fact equilibrium states, provided they remain static. If a defect state were not an equilibrium state, the solid could perform work on the environment without altering the constraints. Performing work is possible only by compensating it with a decrease in the internal energy of the solid, which is tantamount to obtaining work by cooling a system. This contradicts the second law, which prohibits perpetual-motion machines of the second kind. Therefore, defect states must be equilibrium states.

Upon analyzing the examples above, we find that the information of positions of all the constituent atoms, \( \{ R_j \}_{j=1}^{N_a} \), where \( N_a \) is the number of atoms, is required for describing the equilibrium state of a solid. At finite temperature \( T \), the positions of atoms in a solid strongly vary with time \( t \) around their equilibrium positions. An instantaneous position \( R_j(t) \) cannot be a TC because it does not give a unique value for each equilibrium state. Only the time-averaged value \( \bar{R}_j \) is unique. Therefore, the time-averaged atom positions \( \{ \bar{R}_j \}_{j=1}^{N_a} \) can be the TCs for a solid. Moreover, these variables form a complete set of TCs that fully describe the thermodynamic properties of the solid. A more detailed discussion of this subject is available in [5].

The above argument does not depend on the type of structure of the solid. Whether it has a periodicity of a lattice is irrelevant. If we take snapshots of a gas and a glass, the atomic arrangements within the gas and the glass have the same sense of ‘randomness’ in each snapshot. However, for a gas, the instantaneous positions of atoms are irrelevant to the thermodynamic properties of the gas. For a gas, time-averaging the atom positions in equation (2) destroys entirely the distinguishability of atom positions, leaving only the volume as a relevant quantity for thermodynamic properties. We can say that missing information occurs in terms of information theory [23–25]. Conversely, for the glass case, time-averaging does not destroy the distinguishability of atom positions. The correlation between different atom positions \( R_j \) and \( R_i \) does not change with time. This fact explains why it makes sense to describe the thermodynamic properties of a glass by using the time-averaged atom positions \( \bar{R}_j \) as the TCs.

2.1.2. Timescale issues

Let us identify two types of equilibria, which are needed in what follows. System A interacts with the environment in two ways: thermal interactions by exchanging heat \( Q \) and mechanical interaction by exchanging work \( W \), as described by equation (1). When an interaction with the environment is turned on, the state of the system changes toward a new state. When the state of the system ceases to change, the system is called thermodynamic equilibrium, which is defined by definition 1. The time required for no further heat and work exchanges are called the thermal relaxation time \( \tau_t \) and mechanical relaxation time \( \tau_m \), respectively. As these relaxation times are the same order of magnitude, they need not be distinguished in typical cases. However, in this study, the distinction becomes important.

In this study, nonequilibrium states of a solid are also investigated in special circumstances. As shown in the next subsection, the \( \tau_t \) in solids is very short; hence, the phonon subsystem almost immediately equilibrates. Thus, the temperature \( T \) is unambiguously determined. Conversely, because the variations of the mechanical part are often slower than \( \tau_t \), when taking the period \( t_0 \) of time averaging in equation (2) to be of the order of \( \tau_t \), we have a well-behaved function \( \bar{R}_j(t) \) at each moment. This can be a TC, although it has time dependence. In this study, this state is called temporal equilibrium. In the usual context of thermodynamics, the term quasistatic state may be used for temporal equilibrium. However, quasistatic state normally implies a reversible process, while slow but irreversible processes have to be treated here.

Constraint is a theoretical device to idealize energy barriers. It perfectly inhibits the change in a ‘go or no go’ manner (see page 10 in [26]). However, because all energy barriers in real solids are finite, we can only speak of equilibrium within a given relaxation time. In many applications, the distinction between stable (global) and
metastable (local) equilibrium states is useful. However, in the present context, this distinction is not important because every equilibrium is defined only in a relative sense. For example, a gas mixture of nitrogen and hydrogen is stable at ambient temperature but, in astronomical time, it will become ammonia gas. If nuclear reactions are considered, then nothing is stable except protons and electrons. Each constraint \( \xi \) is thus associated with an energy barrier, which determines the corresponding relaxation time \( \tau_\xi \). The mechanical relaxation time \( \tau_m \) is used as presenting collectively a set of \{\( \tau_\xi \)\}.

### 2.2. Hierarchy of thermodynamics in solids

#### 2.2.1. From solid-state theory to thermodynamics

Thermodynamics itself does not provide recipes for deriving the formula for the internal energy \( U \). This task falls to microscopic theories. Today, the most reliable method to calculate the energy of solids at \( T = 0 \) is density-functional theory (DFT) [27–29]. The ground state of a given solid is uniquely determined by the electron density \( \rho(t) \) for a given external potential. For numerous problems of solids, the adiabatic approximation holds [30]. Electronic and atomic coordinates are decoupled, because of the large difference in their masses. Based on this approximation, DFT restates that the ground-state energy \( E_{\text{gs}} \) of a solid is uniquely determined by the positions \{\( \mathbf{R}_i \)\}_{i=1,...,N} of the atoms that comprise the solid. The ground-state energy \( E_{\text{gs}} \) can be expressed as a function \( E \) of the atom positions,

\[
E_{\text{gs}} = E_{\text{gs}}(\{\mathbf{R}_j\}).
\]  

(3)

This relationship is valid even when atoms are not in their equilibrium positions; otherwise, virtually all \textit{ab initio} molecular-dynamics simulations would lose their rigorous grounding. The ground-state energy \( E_{\text{gs}}(t) \) of a solid at the present time is uniquely determined solely by the present positions \{\( \mathbf{R}_j(t) \)\} of atoms, irrespective of their past history.

At finite temperature, atoms in a solid undergo rapid motion about their equilibrium positions, \( \mathbf{R}_j(t) = \mathbf{R}_j + \mathbf{u}_j(t) \), where \( \mathbf{u}_j(t) \) is a small displacement from the average position \( \mathbf{R}_j \). In the harmonic approximation, \( E_{\text{gs}}(\{\mathbf{R}_j(t)\}) \) can be expanded as

\[
E_{\text{gs}}(\{\mathbf{R}_j(t)\}) = E_{\text{gs}}(\{\mathbf{R}_j\}) + (1/2) \sum_{i,j} k_{ij} u_{ij}(t) u_{ij}(t),
\]

where \( k_{ij} \) are the force constants and the Cartesian coordinates are absorbed in the indexes \( i \) and \( j \). Upon adding the kinetic energies of the atoms, the total energy \( E \) of a solid is obtained as

\[
E(t) = E_{\text{gs}}(\{\mathbf{R}_j\}) + (1/2) \sum_{i,j} M_i \dot{u}_{ij}^2(t) + (1/2) \sum_{i,j} k_{ij} u_{ij}(t) u_{ij}(t),
\]

where \( M_i \) is the mass of the \( i \)-th atom. The characteristic time of atomic motion in solids is the phonon period \( \tau_{\text{ph}} \), which is of the order of 10 fs. Although this timescale is very short, it is longer than the response time of electrons, so that the thermal properties of solids can be described by DFT, despite it being a zero-temperature theory. By averaging over a timescale much longer than \( \tau_{\text{ph}} \), the averaged energy, that is, internal energy \( U \), is given by

\[
U = \bar{E}(\{R_j\}) = E_{\text{gs}}(\{\mathbf{R}_j\}) + \frac{1}{2} \sum_k \omega^2_k q^2_k,
\]

(4)

where \( q_k \) is the amplitude of the \( k \)-th normal mode of frequency \( \omega_k \). Normal modes \( \{q_k\} \) are obtained by a unitary transformation of displacements \( \{u_i\} \), so \( U \) is expressed as

\[
U = U_\ell(\{\mathbf{R}_j\}) + U_\ell(\{\mathbf{u}_j\}).
\]

(5)

The first term \( U_\ell \) on the right-hand side is the potential part of \( U \), which corresponds to the first term in equation (4) and is called the structural part here. The second term \( U_\ell \) is the kinetic part of \( U \), which corresponds to the second term in equation (4) and is called the phonon part.

The temperature dependence of \( U \) stems from the phonon amplitude in the form

\[
\frac{1}{2} \omega^2_k q^2_k = (1/2 + \tilde{n}_k) \hbar \omega_k,
\]

where \( \tilde{n}_k \) is the Bose occupation number, which is given by

\[
\tilde{n}_k = \left( e^{\hbar \omega_k/k_B T} - 1 \right)^{-1} \quad (\text{Planck’s constant and } k_B \text{ is Boltzmann’s constant}).
\]

The phonon frequency \( \omega_k \) is determined by force constants \( k_{ij} \), which in turn are determined by the curvature of \( E_{\text{gs}}(\{\mathbf{R}_j\}) \) with respect to \( \mathbf{R}_j \). Accordingly, \( U_\ell \) is a function of \( T \) and \{\( \mathbf{R}_j \)\}, that is, \( U_\ell(\{\mathbf{u}_j\}) = U_\ell(T, \{\mathbf{R}_j\}) \). Because the force constants usually depend only weakly on \{\( \mathbf{R}_j \)\}, we can ignore this dependence. Consequently, the variables may be separated as follows:

\[
U = U(T, \{\mathbf{R}_j\}) = U_\ell(T) + U_\ell(\{\mathbf{R}_j\}).
\]

(6)

When we measure the specific heat of solids, we normally obtain only the phonon part \( U_\ell \), in addition to the small contribution from the volume expansion. During phase transitions of crystals, \( U_\ell \) appears as latent heat, so the structural part \( U \) is not detected in specific-heat measurements. Usually, phase transitions occur on a timescale of the order of 1 ns. This structural relaxation time \( \tau_s \) is longer than \( \tau_{\text{ph}} \) but remains very short compared with experimental timescales. Hence, normal crystallization-melting phase transitions are reversible even though the transition time is very short in our sense.

#### 2.2.2. Fundamental relation of equilibrium

To obtain the fundamental relation of equilibrium (FRE), we must know entropy \( S \). It is elemental to calculate \( S \) for a solid using the harmonic approximation:
\[ S = S([\mathbf{R}_j]) = \sum_k \{(\bar{n}_k + 1)\ln(\bar{n}_k + 1) - \bar{n}_k \ln \bar{n}_k \}. \tag{7} \]

By inverting \( T \) in equation (6) to \( S \), we establish the FRE for a solid,

\[ U = U(S, \{\bar{R}_j\}). \tag{8} \]

The entropy arising from phonons is hereafter denoted as \( S_\text{s} \). If desired, the volume \( V \) can be extracted from a set \( \{\mathbf{R}_j\} \), and \( V \) may be explicitly included as a TC. However, this variable is not of interest here and so is omitted from the following argumentation. We have thus established the following theorem:

**Theorem 1 (Properties of thermodynamic equilibrium).** The thermodynamic properties of a solid that is in thermodynamic equilibrium are uniquely determined solely using the time-averaged present positions \( \{\bar{R}_j\} \), irrespective of their past history.

The adjective ‘present’ preceding the word positions should be stressed. If this adjective was absent, thermodynamics could not be applied to solids because a state in the thermodynamic context must be independent of the process in which it was obtained. It is nonsensical to claim that the properties of a glass state depend on the process. Properties are states in the thermodynamic context [7]. Obtaining different properties is achieved only because samples with different structures were obtained depending on the conditions of preparation. If two samples possessing the same properties are obtained, these two samples must be identified as the same state even if they were obtained using different processes. In this manner, the glass state becomes a well-defined thermodynamic state.

### 2.2.2.1. Alternative expression of the fundamental relation of equilibrium

All the properties of a solid in thermodynamic equilibrium are determined by the FRE (8). Any property \( Y \) is given by a function of TCs as \( Y = Y(S, \{\bar{R}_j\}) \). Because \( Y \) is a function of many variables, it is generally not invertible. Nonetheless, properties can be used as TCs, instead of \( \{\bar{R}_j\} \). For example, internal energy \( U \) is a function of \( \{\bar{R}_j\} \). The relation between them is one to many. However, \( \{\bar{R}_j\} \) can be grouped together according to the value \( U \). Let us denote \( \{\bar{R}_j\}_U \) as a set of atom configurations that yield the same \( U \). In this manner, a one-to-one correspondence between \( U \) and \( \{\bar{R}_j\}_U \) can be found. Within this grouping, \( U \) can be used as a TC,

\[ (T, \{\bar{R}_j\}) \rightarrow (T, U). \tag{9} \]

Now, \( T \) and \( U \) are two independent variables, whereas for gas states one of the two is a dependent variable. The use by Bridgman of both stress and strain as independent variables [2] is supported on these grounds. If each set \( \{\bar{R}_j\}_U \) can be further grouped into subsets \( \{\bar{R}_j\}_{U,Y} \), another property \( Y_2 \), a set \( (T, U, Y_2) \) forms a three-dimensional state space. In this manner, we can construct an unlimited-dimensional state space spanned by \( \{T, U, Y_2, Y_3, \ldots\} \).

### 2.2.3. Adiabatic approximation of the second kind

For glasses, an interesting situation occurs; namely, a large separation occurs between two relaxation times of \( \tau_i \) (\( \approx \tau_g \)) and \( \tau_s \). The structural change in the glass transition occurs over a time longer than 1 s. This significant difference between \( \tau_i \) and \( \tau_s \) simplifies the treatment of glass transition, contrary to the common belief that treating glass transition is complicated owing to its nonequilibrium nature. Two types of motions can be treated separately. We call this separation the adiabatic approximation of the second kind. The time development of the averaged atom position \( \bar{R}_j(t) \) is adiabatically separated from its time-averaged displacement \( \bar{u}_j \) around \( \bar{R}_j \).

This approximation implies that the equilibrium of the phonon part of the system is maintained at each moment of the structural change; thus, the temperature of a glass is well defined at each moment. Therefore, the state of a glass substance in the glass transition is a temporal-equilibrium state. Equation (6) is now written as a function of time \( t \),

\[ U(t) = U_j(T(t)) + U_f([\bar{R}_j(t)]), \tag{10} \]

where time \( t \) in the equation is in the timescale considerably longer than \( \tau_i \) is understood. In this respect, all previous studies are the same as the present theory; the existence of \( T(t) \) at each moment is taken for granted. Experimentalists can easily measure a temporal value \( T(t) \) during a glass transition. On the other hand, glass researchers are mainly interested in the behavior of a glass substance during glass transition, where the observed time is comparable to or even shorter than \( \tau_s \). Therefore, thermodynamic equilibrium is not established and the observed changes are nonequilibrium states; accordingly, the transition is irreversible unless handled with special care. The change in the structure depends on the rate of temperature variation, \( \gamma = dT/dt \). From equation (10), specific heat has both components of the phonon part \( C_\text{s} \) and the structural part \( C_\text{f} \):
\[ C(t) = C_s(t) + \frac{1}{\gamma} \sum_j \left( \frac{\partial U_j}{\partial \mathbf{R}_j} \right) \frac{d\mathbf{R}_j}{dt}, \]

where \( C_s \) is given by

\[ C_s(t) = \sum_j \left( \frac{\partial U_j}{\partial \mathbf{R}_j} \right) \frac{d\mathbf{R}_j}{dt}. \]

The entropy \( S \) must be handled with care. From the fundamental standpoint, whether entropy can exist for nonequilibrium states and how to define it if exists have long been notorious problems in statistical mechanics \cite{31-38}. In equation (2), the value of entropy depends on the period \( t_0 \) over which the time average is considered: the value cannot be uniquely determined. Treating this big problem is beyond the scope of the present study. This difficulty, however, does not arise when the adiabatic approximation of the second kind holds. In this case, the number of microstates is countable (enumerable) in terms of the number of configurations, irrespective of the period \( t_0 \) of averaging. \( S(t) \) is a smooth function of \( t \) in a timescale of \( \tau_r \).

Now, the dimensionality of the state space, which is spanned by \( \{ \mathbf{R}_j \}_{j=1,...,N} \), has a role. A reversible change produces no entropy, so the dimensionality \( M = N_a \) does not change. Because none of the TCs \( \{ \mathbf{R}_j \}_{j=1,...,N_a} \) are missing, we can, in principle, trace all coordinates \( \mathbf{R}_j(t) \). The time dependence in \( S(t) \) is contributed solely by the phonon part \( S_\text{p}(t) \); the mechanical part \( S_\text{m}(t) \) carries no entropy production. This category includes elastic oscillation of a solid, which is reversible despite the fast changes on laboratory timescales. In contrast, irreversible changes, such as interdiffusion of atoms at a junction between different metals, do produce entropy. The position of a diffusing atom \( \mathbf{R}_j(t) \) is then missing from the set of TCs. Information is lost through reduction of the dimensionality \( M \). In [5], this reduction is called degeneration of the state space. Degeneration of the state space corresponds to an increase in the configuration entropy, which is here called the structural part \( S_s \).

Spontaneous changes in the structure are irreversible; a large number of atom configurations appear and the number of these configurations increases with time. In principle, atom configurations \( \{ \mathbf{R}_j(t) \} \), where \( K \) is the label for atom configurations, are identifiable at each moment. However, only those atoms that do not change their equilibrium positions are qualified as TCs. There are \( W_\text{c}(t) \) ways for an atom configuration \( K \). Upon normalizing by the total number of configurations, we obtain the distribution function \( P_K(t) \) of atom configurations. The contribution of the structural part to entropy \( S_s \) is then obtained as

\[ S_s(\{ \mathbf{R}_j^K(t) \}) = -\sum_K P_K(t) \ln P_K(t), \tag{13} \]

where \( (K) \) is the collective label of configurations. The total entropy \( S \) at time \( t \) is thus obtained as

\[ S(t) = S(U(t), \{ \mathbf{R}_j^K(t) \}) = S_s(U(t)) + S_s(\{ \mathbf{R}_j^K(t) \}). \tag{14} \]

Equation (14) says that the entropy \( S(t) \) of a solid at the present time is determined by the present distribution \( \{ P_K(t) \} \) of atom configurations \( \{ \mathbf{R}_j^K(t) \} \). By combining equations (10) and (14), we obtain

\[ U(t) = U(S(t), \{ \mathbf{R}_j^K(t) \}). \tag{15} \]

Now, not all of the atom positions are TCs. The probabilistic nature of entropy mixes different atom configurations.

**Theorem 2 (Properties of temporal equilibrium).** The thermodynamic properties of a solid that is in temporal equilibrium are uniquely determined solely by one of the representatives of the groups of present atom configurations \( \{ \mathbf{R}_j^K(t) \} \), irrespective of the past history.

Entropy thus becomes a well-defined quantity even in nonequilibrium states. However, this is not to say that everything is the same as for equilibrium states. In a temporal equilibrium, the current entropy \( S(t) \) is not at the maximum under the given constraints. The maximum-entropy principle states that, for a fixed \( U \), the equilibrium state is reached when the total entropy \( S \) reaches its maximum [21]. This requires

\[ T_s = T, \tag{16} \]

where \( T_s = \partial U / \partial S_s \) is the phonon temperature and, therefore, the true temperature \( T \), whereas \( T_s \) is merely a parameter defined by \( T_s = \partial U / \partial S_s \).

Note that the configuration entropy can also exist in equation (8). However, because constraints fix the atom positions \( \{ \mathbf{R}_j \} \), changing atom configurations is virtually inhibited; the configurations have no consequence on the thermodynamic properties of that state. Using the wording of [5], those coordinates are called frozen coordinates.
2.2.3.1. Internal variables
The existence of the FRE of equation (15) is tacitly assumed in most of the previous theories on nonequilibrium phenomena in solids, although the background ideas are different. These theories assume the existence of \( T(t) \) at each moment. Thermodynamic functions, such as free energies, are defined for each time of the change. However, additional TCs are required to describe the change in the structure. Traditionally, additional parameters called internal variables \( Z \) (or order parameters) are introduced to describe nonequilibrium phenomena. The idea came from the treatment of chemical reactions in gases, where the advancement of the reaction indicates how the reaction has progressed [39]. The advancement of the reaction is a dynamical variable describing the process and is not a TC; this is applied to gas reactions for which two relaxation times \( \tau_1 \) and \( \tau_2 \) do not differ significantly.

Various internal parameters are used in the glass literature [40–43]. Among them, the fictive temperature \( T^* \) is the most commonly used internal variable [10, 12–14, 44]. The fictive temperature is a parameter that reflects the instantaneous structure of a glass. Therefore, it is reasonable to assume that \( T^* \) is a function of atom positions: \( T^* = T^*(\{R_i\}) \). As discussed in section 2.2.2, a property \( Y \) of a material can serve as a TC of the material. Therefore, when the adiabatic approximation of the second kind holds, \( T^* \) can be used as a TC. Theorem 2 gives a rigorous base for the idea of fictive temperature. Similarly, enthalpy \( H \) can be used as a TC. Later, \( H \) is used to analyze the \( C-T \) curve of glasses. One problem of the fictive temperature is to know what state this temperature refers to. This problem is discussed in section 3.3.

2.2.3.2. Potential-energy landscape
The method of the potential-energy landscape (PEL) is widely used to study glass physics [42, 45, 46]. Several features are common to the PEL method and the present theory. First, in the PEL method, the system is described by the potential, which is a function of all atom positions, \( V(\{R_i\}) \). This is consistent with theorem 1. The potential of a glass has many local minima called basins. Second, in the PEL method, the thermal average is obtained by using a partition function,

\[
Q = \sum_{\{R_i\}} \Omega(\{R_i\}) e^{-\beta \Delta V(\{R_i\})} = \sum_i \Omega(e_i) e^{-\beta f(e_i, T, V)},
\]

with an appropriate normalization factor. Here, \( e_i \) is the energy minimum of basin \( i \), \( \Delta V(\{R_i\}) = V(\{R_i\}) - e_i \), \( f(e_i, T, V) \) is the free energy of basin \( i \), \( \Omega(e_i) \) is the number of basins of depth \( e_i \), and \( \beta \) is inverse temperature. The summation is considered over all basins. The use of the partition functions is tantamount to assume thermal equilibrium because the parameter \( \beta \) have sense only for this case. This treatment is consistent with the adiabatic approximation of the second kind in the present theory. A difference between the two methods is that in the PEL method, \( V(\{R_i\}) \) is treated as being independent of \( T \), whereas it is not in the present theory. After integrating over all \( \{R_i\} \), \( Q \) in equation (17) becomes a function only of \( T \) and \( V \). It follows that all thermodynamic quantities derived from \( Q \) are functions only of \( T \) and \( V \). However, it is unrealistic to consider that the potential does not change during the glass transition. The transition is defined by the change of structure.

To adapt this statistical treatment to the glass transition, the effective temperature \( T_{\text{eff}} \) is introduced as

\[
Q = Q(T_{\text{eff}}, T, p) = \sum_i \Omega(e_i) e^{-\beta_{\text{eff}} f(e_i, T, p)},
\]

where \( \beta_{\text{eff}} \) is the inverse of \( T_{\text{eff}} \). Only when equilibrium is established do we have \( T_{\text{eff}} = T \). Although the phenomenological introduction of \( \beta_{\text{eff}} \) brings about useful results for many problems of glasses, this parameter is not justified on physical grounds [42].

3. Glass state and glass transition

3.1. The glass-transition temperature in C-T curve
We now discuss the glass transition. The glass transition is observed in a narrow range of temperatures in the \( C-T \) curve, as shown in figure 1. The specific heat \( C_g \) of the liquid state is generally greater than that of the solid state \( C_s \). When a supercooled liquid of a glass substance is cooled, the specific heat of the liquid begins to rapidly decrease at the temperature \( T_g \). This rapid decrease ceases at \( T_g \), which indicates the termination of the solidification process. Below \( T_{g,1} \), the glass substance is in the solid state: the term ‘glass state’ is used herein in this restricted sense. In the range \( T_g < T < T_{g,2} \), the state of the glass substance is referred to as the transition state. Although the definition of the glass-transition temperature \( T_g \) within the width \( \Delta T_g = T_{g,2} - T_{g,1} \) is somewhat arbitrary [47], this does not matter for this study.

The \( C-T \) curve depends on the heating and cooling rate, so \( T_g \) varies based on the preparation conditions. This fact leads some researchers not to regard \( T_g \) as an inherent property of glasses [15, 48–50]. However, the change in \( T_g \) is only slight; for glycerol, a one-week prolongation of the transition state altered the \( T_g \) by only
several degrees [51]. $T_g$ has a physical significance in the same degree as the melting temperature $T_m$ does in crystalline materials. The term *kinetically frozen* frequently used in the glass literature hinders the generic role of the kinetics in solidification. Any solidification is a kinetically frozen process, in which the energy gain due to the potential part overcomes the entropic gain of the kinetic part. In crystals, the melting temperature $T_m$ is determined by the balance between the potential part $\Delta H_m$ and the kinetic part $T_m \Delta S_m$ of the free energy in the form

$$\Delta H_m = T_m \Delta S_m, \quad (19)$$

where $\Delta H_m$ is the enthalpy of fusion and $\Delta S_m$ is the entropy of fusion. The latter is essentially the configurational entropy $S_c$ of the liquid. For glasses, there is a well-known formula by Adam-Gibbs formula for the temperature dependence of viscosity $\eta$ around $T_g$,

$$\eta = A' \exp \left( \frac{B' \Delta \mu}{T S_c} \right), \quad (20)$$

where $A'$ and $B'$ are constants and $\Delta \mu$ is the potential barrier for atom rearrangement [48]. By considering that the glass transition occurs near $\eta \approx 10^{13}$ Poise, we can consider equation (20) as the condition of the glass transition. By choosing appropriate values for the constants $A'$ and $B'$, equation (20) becomes $\Delta \mu = T_g S_c$, which has the same form as equation (19).

The dependence of $T_m$ on the preparation conditions is not specific to glass only. The theory of crystal growth tells us that supercooling is indispensable for complete crystallization, no matter how small the effect is [52]; otherwise, the crystallization process would require an infinite time. For the graphite-diamond system, the transition curve between these two phases has been established [53]. However, deviations from the transition curve are often observed owing to the kinetics of the transition. Moreover, diamonds can be synthesized even at low pressures [54, 55]. A recent study shows that the kinetics of reaction agents drastically changes the phase boundary of boron crystals [56].

The curve in figure 1 is produced by a heat cycle starting from the liquid state, cooling to the glass state, and then heating to restore the liquid state. After completion of a heat cycle, the enthalpy $H$ returns to its initial value, so the following relation holds:

$$\oint C dT = 0. \quad (21)$$

Generally, this closed relation is not guaranteed when a heat cycle consists of starting from the glass state, heating to the liquid state, and cooling to the glass state. This says that the final state of the heat cycle differs from the initial state. Despite this, the specific heat $C_g$ of the glass state remains the same. Note that although the closed relation (21) holds when the initial and final states are the same, the closed relation does not necessary hold for $S$. When hysteresis appears in the C-T curve, the heat cycle is irreversible, resulting in the Clausius inequality $\oint C d \ln T < 0$. 

![Figure 1. Glass transition observed in the specific heat C. The cooling and heating processes are indicated by arrows.](image-url)
3.2. Glass state

3.2.1. Equilibrium nature of glass state

Presently, the conventional view holds that the glass state is far out of equilibrium. However, this argument overlooks the role of constraints described in section 2: equilibrium holds only under given constraints. To understand this, consider water in a container, which is in a stable equilibrium, irrespective of the elevation the container is held at. However, if a hole punctures the container, the water immediately flows out to the ground. The state of water in the elevated position is quite unstable. The constraint (i.e., the wall of the container) thus renders stable an otherwise unstable state. In a similar manner, the energy barriers built around the atoms render stable an unstable structure of a glass. Based on theorem 1, the glass state is an equilibrium state because the positions of all atoms are fixed. Furthermore, multiple reasons explain why the glass state is an equilibrium state, as detailed below.

To begin with, viewing the glass state as an equilibrium state is compatible with the zeroth law of thermodynamics, which defines temperature in terms of equilibrium between two systems. Of course, the temperature of a glass can be measured by usual methods. No change occurs when a glass at temperature $T$ comes in thermal contact with another system at the same $T$. This by no means a trivial matter. If glass was not an equilibrium state, work could be extracted from it without changing other conditions. This is tantamount to extracting work from only one heat bath, which contradicts the second law of thermodynamics.

Second, note that the belief that glass will crystallize if given sufficient time is merely speculation about future events. In mechanics, if a stone rests on a slope, we regard that this state is an equilibrium state. The interpretation is that equilibrium is established by the frictional force canceling the gravitational force exerted on the stone. However, given sufficient time, the stone may move downward. If we were to regard the stone to be in a nonequilibrium state based on its future event, nothing could be claimed with certainty. We can thus speak of equilibrium only within the constraints that are valid at the present time.

Third, the view of glass as a nonequilibrium state conflicts with observed facts. A current observation is that glasses can maintain their structure for over one million years [17, 57], whereas over a similar time span, most metals degrade due to corrosion, oxidation, and other effects.

3.2.2. Reconciliation with the third law of thermodynamics

The belief that the glass state is a nonequilibrium state arose for historical reasons. Nonvanishing entropy at $T$ close to zero was found in glass materials in the early 20th century [9, 58], which contradicts the third law of thermodynamics. Researchers resolved this problem by deeming that the glass state was out of equilibrium. They considered that thermodynamics is a theory for equilibrium states only, and that glasses are therefore not subject to the laws of thermodynamics (see, e.g., [59], p.63). This is not true. The issue of the third law of thermodynamics is deeply related to the definition of equilibrium and was solved in previous work [60]. Here, only the main results are summarized, and readers are referred to [60] for more details.

The statement of the third law of thermodynamics is that two materials have a common origin in entropy $S$ at $T = 0$ when the dimensions of the state spaces of the two materials are the same. When the state spaces have different dimensions, their origins generally differ by a finite amount, and this difference appears as the residual entropy. The TCs that are not common to both materials are the frozen coordinates, which do not influence the thermodynamic properties of the materials (Theorem 1). Thus, the entropy of a particular sample of glass can be taken as $S_0 = 0$ at $T = 0$, because the particular sample occupies only one atom configuration $K$. When we compare the entropy of a glass state with that of a crystal state, their respective origins must be adjusted, because the dimensions of the state spaces are different. This is possible only by removing the constraints that maintain the frozen coordinates. At this moment, the glass turns out to be in a nonequilibrium state, which must change toward the equilibrium state, which may be the crystal state. Upon reaching the final state, the entropy difference vanishes, and the third law of thermodynamics is recovered. Thus, the problem of residual entropy does not conflict with the third law of thermodynamics.

3.2.3. Randomness and order parameter

A misconception of randomness makes understanding the nature of glass more difficult. Unfortunately, even now the literature mistakes the absence of periodicity for disorder, despite the caution urged by several authors [23, 25, 35, 61, 62]. A lack of periodicity does not necessarily imply disorder. The structure of DNA has no periodicity, but yet the entropy is very small. Our town has geometrically no regularity. Despite this, a postman can correctly deliver postal materials to any address, if he has a town map. The distinction between order and disorder is made by whether information is missing. As discussed in section 2.1, in spite of the apparent randomness, the information about the atom position in a glass is not destroyed by averaging over time. This is reflected in the specific heat of a glass, which is not so much different from that of its crystal phase [63–66]. This means that the entropies of the two phases have similar values, besides the residual entropy, which is deactivated because of the frozen coordinates.
Based on the entropy, the degree of order of the glass state is similar to that of the crystal, provided the frozen coordinates are disregarded. In this sense, the TC is akin to an order parameter. Since the notion of the order parameter was introduced for describing the glass transition by the pioneering work of Davies and Jones [44], discussion has continued on the nature of the order parameter of glasses [15, 17, 67–71]. The elusive notion of order in disordered materials has yielded various definitions of the order parameter. We now see that the order parameter is no more than a TC. Any property $Z$ that is characterized by the structure, $Z = Z(\{R_j\})$, can be used to indicate the order of glasses.

3.3. Transition state of glass

An important issue regarding the nature of the glass state lies in the interpretation of the transition region of a $C$-$T$ curve. As is already repeated, there is no doubt that glass transitions are nonequilibrium phenomena. Despite this, thermodynamics methods are not invalidated if the adiabatic approximation of the second kind holds, as described in section 2.2.3. This is the case for the transition region. We can treat the structural and phonon parts of atom coordinates separately and treat the phonon part as being in thermal equilibrium. The structural part conveys irreversibility because it involves relaxation processes, which is responsible to the hysteresis. Correct understanding of the relaxation processes is essential.

The $C$-$T$ curve is affected by the preparation conditions, in particular by altering the cooling and heating rate $\gamma$. An interesting question about the glass transition is toward what state does the glass transition. It is generally considered that glass finally transitions to the supercooled-liquid state if given sufficient time. In the literature, this is explained by extrapolating the supercooled-liquid state. Figure 2 is a $H$-$T$ curve often used for the explanation [10, 72–74]. This curve is obtained from a $C$-$T$ curve by integrating $C(T)$ with respect to $T$. The following explanation is based on the study of Davies and Jones [10, 44].

A glass state is obtained by cooling a supercooled-liquid state of a glass substance. The enthalpy $H$ of supercooled liquid is indicated by line AB. The low-temperature part of AB is a linear extrapolation of the high-temperature part of the $H$-$T$ curve. The supercooled-liquid state is considered an equilibrium state over the entire range of $T$. The ideal glass should appear on this extrapolated line. When cooled to a temperature slightly below $T_{g,2}$, $H$ of the glass substance begins to deviate from the equilibrium line AB. As $T$ decreases further, the deviation increases. At a point D ($T_{g,1} < T_D < T_{g,2}$), we stop the cooling and detach the system from the heat bath. A relaxation process begins toward the equilibrium state AB. If we wait sufficiently long, the supercooled-liquid state will be recovered. This is the view that most researchers envisage.

However, no evidence exists to indicate that the stability of the supercooled-liquid state at $T > T_{g,2}$ can be extrapolated to lower temperatures. This is merely a speculation. An excuse for the lack of evidence is that the time required to reach equilibrium is extremely long for accessing by experiment. The reason for the stability of the supercooled liquid is thus largely based on the concept of ergodicity, which claims that every atom of a glass substance in equilibrium visits every position inside the glass. The high viscosity of glass, however, prevents the atoms from visiting everywhere except the vicinity of their initial position. This reasoning has pervaded the

![Figure 2. Enthalpy $H$ versus temperature $T$ in the glass transition. Cooling and heating processes are indicated by arrows. Note that two curves for cooling and heating processes are obtained for the two samples, which had different heat treatments.](image-url)
research of glass for over a century. However, this is a one-sided argument, which overstates the role of ergodicity. Thermodynamic equilibrium is established by two competitive forces: the active tendency and the passive resistance in the words of Gibbs ([21], p.58). The former is driven by ergodicity, whereas the latter is caused by constraints, to use the current terminology. Crystallization is the consequence of overcoming of the constraint over ergodicity, as is already discussed in section 3.1.

The stability of supercooled liquid at $T < T_{g,2}$ is incompatible with the thermodynamic stability of a material, namely, the positive definiteness of specific heat ([7], p 206). The fact that the specific heat is positive ensures that the free energy $G(T)$ is concave with respect to $T$, i.e. $\partial^2G/\partial T^2 < 0$. This says that below the transition temperature, the low-temperature phase must be stable relative to the high-temperature phase. The appendix shows compelling evidence in support of the concave curve of $G(T)$. Therefore, the idea that the transition state transforms into the supercooled-liquid state has never been proven. For the same reason, the transition state cannot be a purely solid glass state in a range $T_{g,1} < T < T_{g,2}$. The transition state is an inhomogeneous mixture of the solid and liquid phases, as is usual for crystallization, where nucleation of solid occurs. The nucleation of the glass state may occur in the transition region [13, 75]. A recent notion of dynamical heterogeneity [15, 16] is consistent with the present conclusion.

Because glasses have many local minima, there is no unique equilibrium state. Depending on the initial configuration $\{ R_j^0 \}$, the glass substance finds a local minimum near the initial configuration. We can operationally define the equilibrium states at $T$ in the transition region as those states that are obtained by cooling as slow at a rate as experimentally accessible. The equilibrium state corresponds to a point on the $C-T$ curve that is obtained by the slowest cooling. This assumption will be used in the next paper.

4. Conclusions

Starting from a rigorous definition of thermodynamic equilibrium and thermodynamic coordinates, this study investigated the thermodynamic nature of glass and its glass transition. The glass state—the solid state in the present context—is an equilibrium state. A glass sample takes one of many possible equilibrium states. The thermodynamic properties of a glass are described solely by the time-averaged positions of its constituent atoms $\{ R_j \}_{j=1, \ldots, N}$. Provided that the constraints that fix the structure are maintained, the freedom of the atom configurations can be regarded as the frozen coordinates that do not contribute to the thermodynamic properties of the glass. Various order parameters, when suitably constructed, can greatly simplify the fundamental relation of equilibrium.

On the other hand, a glass substance in the transition region exists in a nonequilibrium state, as is generally thought. Nevertheless, when the adiabatic approximation of the second kind holds, the thermodynamic properties of the transition state are determined solely by their current thermodynamic coordinates, but with $\{ R_j \}$ replaced by the values of a representative configuration within a group of atom configurations $\{ R_j^{(k)}(t) \}$. Moreover, the current entropy $S(t)$ is not at the maximum under the given set of constraints. The positions of those atoms that move beyond the constraints are removed from the set of TCs. The missing TC information is reflected in the configuration part of the entropy. A significance of the present theory is to demonstrate that the hysteresis in the glass transition can be described by TCs $\{ R_j^{(k)}(t) \}$ through the structure dependence of the energy barrier $E_h(\{ R_j^{(k)}(t) \})$. Complicated history-dependent response functions are unnecessary.

Finally, it was shown that the widely-held view—that the final state of the transition state is supercooled liquid—is incompatible with the positive-definite property of specific heat. The above findings provide a basis for further study on glass-transition phenomena.

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Appendix. Free energy of transition state of glass

This appendix illustrates that the extrapolation of the enthalpy $H$ of a supercooled-liquid state leads to an incorrect conclusion. Consider figure A1(a), which shows a $C-T$ curve of glucose.
Experimental data of the isobaric specific heat \( C_p \) of glucose were taken from \([76](4, \text{ red})\) and \([77](2, \text{ blue})\). The figures for \( C_p \) were obtained by digitizing the curves from these papers. The enthalpy \( H \) and the entropy \( S \) were then obtained by integrating \( C_p \) as
\[
H(T) = \int_{T_0}^T C_p \, dT \\
S(T) = \int_{T_0}^T C_p \, d\ln T,
\]
respectively. The Gibbs free energy \( G \) was obtained similarly. The reference temperature \( T_0 \) was presumed sufficiently high to ensure the liquid phase of glucose; hence, the energy functions were evaluated on different samples with common origins. The original specific-heat measurements were done by heating. The heating rates \( \gamma \) are \( 3^\circ C/h \) for data set 4 and \( 10^\circ C/h \) for data set 2. The two data sets for \( C_p \) are scaled to match each other for the liquid state. Although the cooling rates for preparing the glass states of glucose are not explicitly given, these must be different, because the integration of \( C_p \) over the transition region, equation (21), does not give zero: there is a difference \( \Delta H = 2.8 \text{ cal/g at } T = 250 \text{ K} \). Because data set 2 was obtained by using a faster heating rate, the advent of a hump near \( T_g,2 \) is reasonable.

As shown in both figures A1(c) and A1(d), the free energy \( G \) of the transition state is lower than the extrapolated free energy of the supercooled liquid. This is a consequence of the positive-definite property of specific heat. This is a completely general property of stable material. Of course, it is also true that, at \( T < T_g,1 \), the free energy \( G \) of the glass state is lower than that of both the transition and supercooled-liquid states. The metastability of the glass state has never been proven.

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