Non-equilibrium thermodynamics. III. Thermodynamic Principles, Entropy Continuity during Component Confinement, Energy Gap and the Residual Entropy

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Abstract

To investigate the consequences of component confinement such as at a glass transition and the well-known energy or enthalpy gap (between the glass and the perfect crystal at absolute zero, see text), we follow our previous approach [Phys. Rev. E 81, 051130 (2010)] of using the second law applied to an isolated system $\Sigma_0$ consisting of the homogeneous system $\Sigma$ and the medium $\tilde{\Sigma}$. We establish on general grounds the continuity of the Gibbs free energy $G(t)$ of $\Sigma$ as a function of time at fixed temperature and pressure of the medium. It immediately follows from this and the observed continuity of the enthalpy during component confinement that the entropy $S$ of the open system $\Sigma$ must remain continuous during a component confinement such as at a glass transition. We use these continuity properties and the recently developed non-equilibrium thermodynamics to formulate thermodynamic principles of additivity, reproducibility, continuity and stability that must also apply to non-equilibrium systems in internal equilibrium. We find that the irreversibility during a glass transition only justifies the residual entropy $S_R$ to be at least as much as that determined by disregarding the irreversibility, a common practice in the field. This justifies a non-zero residual entropy $S_R$ in glasses, which is also in accordance with the energy or enthalpy gap at absolute zero. We develop a statistical formulation of the entropy of a non-equilibrium system, which results in the continuity of entropy during component confinement in accordance with the second law and sheds light on the mystery behind the residual entropy, which is consistent with the recent conclusion [Symmetry 2, 1201 (2010)] drawn by us.

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I. INTRODUCTION

A. Irreversibility

In the previous two papers [1, 2], to be referred to as I and II respectively here, we initiated a general statistical mechanical investigation of non-equilibrium systems undergoing irreversible changes during approach to their equilibrium state. It is a very general approach that is not restricted to glasses alone but covers all non-equilibrium situations. In I, we deal with homogeneous systems, while in II we deal with inhomogeneous systems. The approach is truly statistical mechanical in nature, and is based on applying the second law of thermodynamics to an extremely large isolated system, which we denote by $\Sigma_0$; it consists of the macroscopic system $\Sigma$ of interest in a medium denoted by $\tilde{\Sigma}$ containing it; see Fig. 1.

We will use body in this work to refer to any of the three systems. According to the second law, the entropy $S_0$ of an isolated system $\Sigma_0$, which is a sum of the entropies $S$ and $\tilde{S}$ of the system and the medium, respectively,

$$S_0(t) = S(t) + \tilde{S}(t),$$

can never decrease in time [3–8]:

$$\frac{dS_0(t)}{dt} \geq 0.$$  \hspace{1cm} (2)

Any change in the entropy of the isolated system is due to irreversibility, so that $d_iS_0 \equiv dS_0 \geq 0$, and $d_eS_0 \equiv 0$ in the standard notation [1, 2, 9–11]. Even for a body, which is not isolated, $d_iS \equiv dS - d_eS \geq 0$, with $d_eS_0 \neq 0$; indeed, the latter can be of any sign. Two important observations about the entropy $S_0$ are in order for Eq. (2) to have a content:

1. The entropy $S_0$ exists under all conditions; thus it includes the situation when $\Sigma_0$ is not in equilibrium or when $\Sigma$ undergoes a glass transition.

2. The entropy $S_0$ is a continuous function of all its arguments $Z_0(t)$ (see below), not shown in Eq. (2), and the time $t$, which is shown.

What happens inside the isolated system (loss of ergodicity in parts of $\Sigma_0$ due to component confinement, chemical reactions, phase changes, turbulence, viscous deformation inside it, etc.) cannot affect the direction of the inequality, which makes it the most general principle of non-equilibrium thermodynamics [1, 2, 9–11]. All the above entropies, in addition to
FIG. 1: Schematic representation of a system $\Sigma$ and the medium $\bar{\Sigma}$ surrounding it to form an isolated system $\Sigma_0$. The medium is described by its fields $T_0, P_0$, etc. while the system, if in internal equilibrium (see text) is characterized by $T(t), P(t)$, etc.

being an explicit function of time $t$, are also functions of extensive observables and internal variables (see II for more details) that themselves may vary with time. Of the observables, the energy, volume and the number of particles are the most important extensive observables from an experimental point of view. In the sequel to the above two paper I and II, we focus on non-equilibrium thermodynamic principles dictating the behavior of a homogeneous system $\Sigma$, the general way its non-equilibrium entropy should behave during relaxation, the way $S$ is determined in terms of its microstates, and the way $S$ must behave when the system becomes confined to a component of the phase space [12–14] during some interval of time (for example, at a glass transition), and the concept of the residual entropy, the entropy that $\Sigma$ will have at absolute zero. As our interest is in investigating the out of equilibrium properties of $\Sigma$, we will assume throughout this work and as was done in I and II that the medium is in internal equilibrium at all times. As a consequence, $\bar{\Sigma}$ has a well-defined constant temperature $T_0$, pressure $P_0$ and other fields and affinities (see below) at all times. In contrast, the system may have no well-defined temperature, pressure, etc. unless it is also in internal equilibrium, in which case, we will denote their instantaneous values by $T(t), P(t)$, etc.; see I for details. They are usually different from the those of the medium unless equilibrium is reached, which occurs as $t \to \infty$. It was shown in I that $T(t) \geq T_0$ in
a cooling and \( T(t) \leq T_0 \) in a heating experiment, and that

\[
dQ = T(t)dS(t) \equiv T_0d_\circ S(t),
\]

where \( d_\circ S(t) \) represents the entropy exchange with the medium; the irreversible entropy generation or the uncompensated transformation of Clausius and de Donder \([9,11]\) within the system is represented by \( d_1S(t) \equiv dS(t) - d_\circ S(t) \geq 0 \).

**B. Determination of Entropy**

The entropy can now be calculated in principle by using Eq. (3) even when the process is irreversible. As the experimentalist has a control over \( T_0, P_0 \), the entropy can be calculated by varying \( T_0 \), keeping \( P_0 \) fixed. The heat capacity \( C_P \) at constant \( P_0 \) in terms of the enthalpy \( H(t) \) and the volume \( V(t) \) is given by

\[
C_P(t) \equiv \left( \frac{\partial H(t)}{\partial T_0} \right)_{P_0} + \left[ P(t) - P_0 \right] \left( \frac{\partial V(t)}{\partial T_0} \right)_{P_0},
\]

see I, so that

\[
dS(t) = \frac{C_P}{T(t)}dT_0 \begin{cases} 
\leq C_PdT_0/T_0 & \text{in cooling} \\
\geq C_PdT_0/T_0 & \text{in heating} 
\end{cases},
\]

and can be used to obtain the entropy using the standard integration process

\[
S(T_0) = S(0) + \int_0^{T_0} \frac{C_PdT_0}{T(t)} + \Delta S_C \begin{cases} 
\leq S(0) + \int_0^{T_0} C_PdT_0/T_0 + \Delta S_C & \text{in cooling} \\
\geq S(0) + \int_0^{T_0} C_PdT_0/T_0 + \Delta S_C & \text{in heating} 
\end{cases},
\]

where \( S(0) \) is the entropy at absolute zero, and \( \Delta S_C \) represents the sum of all possible discontinuities over the range \((0, T_0)\) mainly due to latent heats at possible first-order transitions; it also includes any possible entropy discontinuity due to component confinement. The above inequalities are a simple extension of is a well-known classic result \([15]\), which has been rederived in our approach. Because of a non-negative heat capacity, the entropy is a \textit{monotonic increasing} function of the temperature:

\[
\frac{\partial S}{\partial T_0} > 0
\]

for all finite temperatures. The presence of an internal order parameter can also be accounted for as we will discuss later. We find that the integral

\[
\int_0^{T_0} C_PdT_0/T_0 > 0
\]
provides an upper bound to the entropy $S(t)$ of the system during a cooling experiment, and a lower bound for it during a heating experiment, when the system is out of equilibrium. The difference in the two bounds, which we will denote by $\Delta S_B(T_0, P_0)$ here, strongly depends on the rates of cooling and heating. The two bounds are exactly identical so that $\Delta S_B(T_0, P_0) \equiv 0$, when the system is in equilibrium. Therefore, $\Delta S_B(T_0, P_0)$ can be used as a measure of the irreversibility when no internal variables (order parameters) are invoked, as was recently done by Johari and Khouri [16]. However, introducing internal variables allows us to obtain the entropy without any error, as we will discuss here, even when the system is out of equilibrium and irreversibility is present so that the thermodynamic entropy can be always calculated, at least in principle. Irreversible entropy generation appears through the internal order parameter in the calculation. This is a well-established approach to non-equilibrium thermodynamics [9–11]; see also [1, 2], which we carefully discuss in Sect. III for the sake of continuity.

C. Non-equilibrium Thermodynamic Principles

We have a thorough understanding of thermodynamic principles (additivity, reproducibility, uniqueness and stability, all defined later) and the statistical entropy for an equilibrium system [3–7]. The situation is not so obvious when the system is out of equilibrium. We wish to examine the conditions necessary for the applicability of these principles to, and obtain the statistical formulation of the entropy of, a non-equilibrium system with the aim to develop a non-equilibrium statistical thermodynamics. While in traditional non-equilibrium thermodynamics [1, 2, 9–11], the entropy of any body is postulated to exist under the assumption of local equilibrium, its actual value and its statistical connection with microstate probabilities is of no interest as only the difference in the entropy has any meaning. The same is also true of the thermodynamics applied to glasses [14, 17–20]. The actual value of $S$ is normally set by imposing additional requirement such as by invoking Nernst postulate of the third law [4, 21, 22]. Our interest here is different. We wish to identify the entropy of a body when it is out of equilibrium using statistical concepts. It should be stated here that the entropy for a body in equilibrium is well understood in equilibrium statistical mechanics [3–6]. Thus, any new attempt to define the entropy for a non-equilibrium state must reduce the the well-known form of equilibrium entropy.
D. Component confinement, Entropy Reduction and the Residual Entropy

1. Component Confinement and the Gap

Phase space confinement at a phase transition such as a liquid-gas transition is a well-known phenomenon in equilibrium statistical mechanics. The component confinement also occurs when the system undergoes symmetry breaking such as during magnetic transitions, crystallizations, etc. In such cases, the confinement occurs under equilibrium conditions, and is well understood. The confinement in phase space can also occur under non-equilibrium conditions, when the observational time scale $\tau_{\text{obs}}$ becomes shorter than the equilibration time of the system, such as for glasses, whose behavior and properties have been extensively studied; see Fig. 2 which is adapted from Fig. 10.2 on p. 442 in [14]. The behavior of the entropies and their consequences for a given cooling rate $r$ have been discussed by us in Ch. 10 in [14], and is based on the energy gap model for glasses discussed there. The form of all these entropies is to ensure that they remain concave functions of the energy. The basic premise of the model is the well-known fact that there exists a gap (an energy gap) between the energies of the perfect crystal and the glass at absolute zero, which is at least as much as $E_K$; it is equal to $E_K$ for the ideal glass. The gap is due to defects that are present in the glass with respect to the perfect crystal that raise the energy or the enthalpy of the former. The additional energy of a glass $E_{NE} - E_K$ in a glass, however, is due to the presence of excitations relative to the ideal glass. It should be observed that the slope of FG at G is infinite to ensure that the energy of the system described by FG is $E_{NE} > E_K$ at absolute zero. The investigation of the energy gap model in [14] is very relevant here as it is this non-equilibrium component confinement during the glass transition that we wish to study in this work. The entropy curve FG in Fig. 2 denotes the entropy of some arbitrary time-dependent non-equilibrium state including glasses, and is shown disconnected from the entropy curve BA0 describing the entropy of the disordered state which includes the liquid and the supercooled liquid. The latter is a stationary metastable state below the melting temperature $T_M$, with the crystal representing the stable state below $T_M$. The entropy of the ordered state, which results in the crystal below $T_M$, is schematically shown by BA0. It is a common practice to call the supercooled liquid as an equilibrium state when the interest is mainly to study non-equilibrium states.
FIG. 2: Schematic form of the communal entropy DACK of the disordered liquid/supercooled liquid and the entropy BA0 of the corresponding ordered crystalline state as a function of the energy; other extensive observables are held fixed. The common tangent to DACK and BA0 gives the inverse melting temperature $T_M$. The entropy of some non-equilibrium disordered state for some non-zero cooling rate $r$ is given by FG, which must strictly lie below in accordance with the second law. It terminates at G at an energy $E_{NE}$, which is strictly higher than the energy (taken to be 0 here) of the pure crystal at absolute zero or the energy $E_K$ at K on DACK. The entropy at G gives the residual entropy $S_R$. Even though we have shown FG disconnected from DACK for some arbitrary non-equilibrium state, it continuously emerges out of the latter at some point C at a temperature below $T_M$ in a glass transition. The portion CG in this case represents the entropy of the glassy state. As the cooling rate becomes slower, CG moves towards CK until it finally merges with it as $r \to 0$. The terminal point K is known as the ideal glass transition where the entropy of the equilibrium supercooled liquid vanishes. As FG moves towards ACK, $E_{NE}$ moves towards the ideal glass energy $E_K$ and the residual entropy continues to decrease until the latter finally vanishes in the ideal glass transition at K. However, for any $r > 0$, $S_R$ remains non-zero due to the presence of excitations in the ideal glass that raises its energy above $E_K$. 


denoted by FG; the terminology is obviously incorrect if we need to bring the crystal into the discussion. As our interest in this work is to mainly study time-dependent non-equilibrium states, we will invariably call the supercooled liquid as the equilibrium liquid, knowing well its limitation. In a glass transition from the supercooled liquid, the curve FG emerges out of BACK continuously at some point C, which is determined by the experimental setup such as the cooling rate \( r \).

As the system is not allowed to probe all the disjoint components in time, it can be investigated by our recently developed non-equilibrium approach in I and II; see for example, Eqs. (3-8). One of the important observations of such systems is the existence of a residual entropy \( S_R \), such as the entropy at the point G in Fig. 2. It is the entropy a glass or a crystal would have at absolute zero, and is related to the possible number of disjoint components in the phase space \([8, 12, 13]\). It is merely a measure of the number of lowest energy microstates of energy \( E_{NE} > E_K \) for a given mode of preparation at absolute zero. The macrostate of the glass or the crystal is a collection of all these microstates along with their probability of occurrence for a given mode; see \([8, 23]\). The mode of preparation determines the energies of these microstates, which need not be the lowest possible energy (such as \( E_K \) for the supercooled liquid if we are concerned with a glass) for the system \([14]\). The lowest possible energy microstates represent the equilibrium macrostate at absolute zero. It should be emphasized that there is no reason for the lowest energy macrostate to be non-degenerate in principle, although it seems to be true for a majority of the systems. Therefore, we will assume in this work that \( S_{eq,K} = 0 \) for the supercooled liquid at K. This is borne out of several exact calculations as discussed elsewhere \([14]\). The system (glass or crystal) can be in any of lowest energy microstates (and not the lowest possible energy microstates) for a given mode of preparation, and the residual entropy is determined by all these microstates \([8]\).

2. Residual Entropy

The existence of a non-zero residual entropy (\( S_R > 0 \)) is very common in Nature, and does not violate Nernst’s postulate, as the latter is applicable only to equilibrium states with a non-degenerate ground state \([4, \text{Sect. 64}]\). Its existence was first demonstrated by Pauling and Tolman \([25]\); see also Tolman \([26]\). In addition, the existence of the residual entropy
has been demonstrated rigorously for a very general spin model by Chow and Wu \[27\]. For ice, the residual entropy was observed by Giauque and Ashley \[28\]. Pauling \[29\] provided the first numerical estimate for the residual entropy for ice, which was later improved by Nagle \[30\]. Nagle’s numerical estimate has been recently verified by simulation \[31, 32\]. The numerical simulation carried out by Bowles and Speedy \[33\] for glassy dimers also supports the existence of a residual entropy. Thus, it appears that the support in favor of the residual entropy is quite strong. We wish to emphasize that what is customarily called the third law due to Nernst, according to which the entropy must vanish at absolute zero, is merely a postulate and not a strict theorem even in equilibrium \[4, 21, 22\]. Indeed, many exactly solved statistical mechanical models show a non-zero entropy at absolute zero. Based on these empirical observations, the residual entropy \( S_R \) at \( G \) in Fig. 2 has been taken as non-zero and positive.

We refer to Fig. 2 to emphasize this point once more. As \( r \) decreases, \( G \) moves not only to the left but also down in the figure. This has the consequence of lowering \( E_{NE} \) and \( S_R \), so that entropy continues to decrease with temperature to ensure stability of the glass. The additional energy or enthalpy due to excitation compared to the ideal glass raises the residual entropy of the glass relative to the ideal glass:

\[
S_R > S_{eq,K} = 0 \text{ for } E_{NE} > E_K.
\]  

(9)

However, it is possible that the residual entropy \( S_R \) at \( G \) remains zero for all \( r \) as if all glasses are identical at absolute zero for any \( r \). Indeed, the situation shown in Fig. 2 has been challenged \[34, 38\], because it is argued that the entropy cannot be estimated correctly in the glass transition region, the region where component confinement occurs, where irreversibility comes into play. This is certainly true, as can be easily seen form Eqs \(6\) and \(60\). While the idea that the irreversibility raises some concern about the inferred values of the entropy is certainly justified, the main point is not whether irreversibility is present; see Sect. VI F. Rather, the question should be: how much of an error does this create in the inferred values of the entropy? Thus, the issue at hand is the magnitude of \( \Delta S_B(T_0, P_0) \). Various estimates support an error that does not exceed more than 5%. Jäckle \[13\] has also calculated the amount of uncertainty in the entropy for glycerol due to irreversibility near the glass transition, and found it to be less than 5%. Gutzow and Schmelzer \[39\] have shown by citing some earlier analysis that the irreversible contribution to
the entropy in the vicinity of the glass transition is small enough to be practically neglected. They also provide a very enlightening historical review of the residual entropy in glasses. Nemilov [40] comes to a similar conclusion by suggesting that the error in $S_R$ is no more than 5%. The conclusion is that there is no appreciable error in using conventional equilibrium thermodynamics by replacing the inequality to an equality in Eqs. (5-6) in studying glasses, a point also made recently by Goldstein [41]. In particular, one can get a highly reliable estimate of the entropy of a glass (GL) or the supercooled liquid (SCL) without using any internal order parameter by the following standard integration process using the measured heat capacity

$$S(T_0) = S(0) + \int_0^{T_0} C_p dT_0 + \Delta S_C. \quad (10)$$

More recently, Johari and Khouri [16] have come to a similar conclusion by reanalyzing experimental data.

3. Entropy Reduction

It has been suggested [34–38] that as a consequence of the component confinement, the system is no longer able to explore in time the entire part of the phase space that would be consistent with the observables (such as the energy) of the system. With this interpretation in mind, and recognizing the fact that the entropy is measured by the volume of the accessible phase space, such as that belonging to a component, it is then argued that the entropy $S$ of the system must undergo a sudden or rapid reduction in its value due to component confinement [38] that is expected to occur at the glass transition, but the experiments are unable to capture this because of the irreversibility. We will call this entropy reduction scenario the unconventional view (UV) of the glass transition in this work. In this scenario, either FG in Fig. 2 remains disconnected from BA0 to account for a sudden discontinuous reduction or touches BA0 at some point C but falls off rapidly from C to give rise to a rapid but continuous drop. In the latter scenario, the portion of FG to the immediate left of C will have to change its curvature so that it will be no longer concave, a point of critical importance that will be discussed at several occasions in this work. It is impossible to continuously join two disjoint concave functions without creating a loss of concavity.

If it happens that the entropy $\tilde{S}$ of the medium concurrently undergoes a sudden or rapid rise by an amount such that it not only compensates the reduction in $S$, but add some more
so that $S_0$ does not decrease, then the rapid reduction in $S$ would not violate the second law for the isolated system as given in Eq. (2). However, in this case also, the irreversible entropy change in the system must still satisfy the second law: $d_t S(t) \geq 0$. Therefore, our third aim is to investigate if such a scenario can be supported by the second law.

Our last goal is to use the second law to investigate the idea of the residual entropy from a statistical point of view and to prove that the situation in Fig. 2 with a non-zero residual entropy is borne out of experiments. This will be in contradiction with the idea of an entropy reduction in the unconventional view. The enthalpy $H$ and the volume $V$ are known to be continuous during the glass transition [14, 17–20]. Thus, any entropy reduction will leave its imprint on the behavior of the Gibbs free energy. Thus, we will also investigate the behavior of the Gibbs free energy in this work.

The other relevant issue, which to the best of our knowledge has not been discussed in the literature so far for unexplained reasons, is whether the experimental data support a non-zero residual entropy even if the irreversibility may be quite appreciable, as would happen in a rapid quench. From above, it is clear that the experimental determination of the residual entropy $S_{\text{expt}}(0)$ invariably yields a non-zero value. We derive later a very simple consequence of the glassy irreversibility in the form of an inequality; see Eq. (60). The inequality clearly supports a non-zero residual entropy, even if the irreversible contribution is appreciable; see Eq. (62). It just happens that in most cases, the irreversible contribution turns out to be minimal. However, the reality of the residual entropy is based not on the minimal irreversible contribution; it is rather based on the inequality in Eq. (60). Thus, the entropy reduction due to confinement in the unconventional view cannot be attributed simply to the presence of irreversibility. Its root-cuse, if it exists, has to be found elsewhere.

### E. Goal and Outline

Our aim in this work is to follow the recently developed non-equilibrium thermodynamics [1, 2, 8] to specifically derive non-equilibrium thermodynamic principles, which should reduce to the well-known thermodynamic principles for equilibrium bodies [4, 5, 26]. We must ensure that these principles do not violate the second law in anyway. We start by assuming the existence and continuity of $S_0$, and follow I and II. The existence assumption should not be surprising as the existence of $S_0$ is required to state the second law for an isolated
system $\Sigma_0$; see Eq. (2). The equality in Eq. (2) occurs only when the isolated system is in equilibrium. We will prove here that the existence and continuity of $S_0$ implies the existence and continuity of the Gibbs free energy \[ G(T_0, P_0, t) = E(t) - T_0S(t) + P_0V(t) \] (11) for the open system $\Sigma$ at fixed temperature $T_0$ and pressure $P_0$ of the medium. (Even though it is not a common terminology, we will use "open" to denote any body that is not isolated in this work.) The continuity of $S_0$ is easily traced to the continuity of microstate probabilities, as discussed in Sect. IV. The second law for the open system reduces to the well-known inequality \[ \frac{dG(t)}{dt} \leq 0; \] (12) the equality occurs when the system achieves equilibrium with the medium; this is exemplified by the curve ACK in Fig. 2. It is evident from Fig. 4 that glass free energies $G_{GL, CV}(T_0)$ and $G_{GL, UV}(T_0)$ approach $G_{SCL}(T_0)$ from above, in conformity with Eq. (12). Thus, their behavior during relaxation is not sufficient to rule out either one as unphysical. On the other hand, the continuity of the Gibbs free energy immediately rules out any discontinuous entropy reduction due to component confinement as discussed above but does not rule out a continuous entropy reduction.

The continuity of the Gibbs free energy also establishes the continuity of the entropy of an open system in internal equilibrium by recognizing that the enthalpy of the system remains continuous at the glass transition. The existence of internal equilibrium still allows irreversible relaxation in the system. We find that as a consequence of the second law, the entropy of the system in internal equilibrium decreases during relaxation, thus validating Eq. (13) and invalidating Eq. (14). The latter requires the entropy to increase during relaxation as shown by the relaxation arrow for $S_{GL, UV}$ in Fig. 3. Thus, the second law supports a continuous entropy $S$ during component confinement. On the other hand, the Gibbs free energies of the two glasses satisfy the second law in Eq. (12). In view of the incorrect behavior of $S_{GL, UV}$, this is a very surprising result. It appears that $S_{GL, UV}(T_0)$ and $G_{GL, UV}(T_0)$ do not have the same content. We will find an explanation of this surprising statement later.

The statement about the continuity of the entropy of the system can be made stronger by removing the requirement of internal equilibrium by obtaining a statistical formulation for
it. However, we only need the above weaker continuity statement to rule out the unconventional view of the entropy during the glass transition and to support Fig. 2. The statistical formulation of the entropy of an isolated system in terms of its microstates is given by Eq. (46) in compliance with the second law and which satisfies the above thermodynamic principles. We then discuss how the entropy is defined for an open system under all conditions in terms of microstate probabilities. This derivation also establishes the existence and continuity of the entropy of an open system by recognizing that the entropy of the medium remains continuous during relaxation. This again establishes that continuity of entropy when component confinement occurs. The continuity of the entropy of a body is a generic feature of a statistical system, and is formulated as one of the thermodynamic principles. Therefore, it should also not come as a surprise that the assumption of the existence of the entropy for non-equilibrium states also forms the cornerstone of the conventional non-equilibrium thermodynamics [9–11]. We then proceed to explain the residual entropy in statistical terms and show that there is no reason for it to vanish. We also show that irreversibility alone cannot justify any entropy reduction.

The layout of the paper is as follows. We briefly discuss the two alternative views of the glass transition in Sect. II which is then followed by a short review of some of the useful concepts and results derived earlier [1, 2, 8] in Sect. III. Non-equilibrium statistical entropy is introduced in Sect. IV and the concept of residual entropy is discussed. We then list and discuss important thermodynamic principles that should be valid for a body in internal equilibrium in Sect. V. Sect. VII is the important section, where we discuss the consequences of the non-equilibrium thermodynamics. We discover in Sect. VII D that the unconventional view is internally inconsistency. The last section contains our conclusions.

II. TWO VIEWS OF GLASSES

A. Conventional Glass View (CV)

The small amount of irreversible contribution to the entropy of glasses does not mean that glasses are in equilibrium (with the surrounding medium); rather, it implies that the fast degrees of freedom in glasses have equilibrated, and the slow degrees of freedom, although not yet equilibrated, are changing so slowly as to be almost unchanged over the observation
time. More details about this point can be found in I. For most glasses, the success of Eq. (10) rests on the premise that within 5% of the residual entropy, as noted above, \( d_i S \simeq d_e S \). As a consequence, \( S(0) \) for a glass in Eq. (10) is correct within 5%; its entire magnitude is only weakly affected by the irreversibility encountered during the glass transition. This view will be called the \textit{conventional view} (CV) of the glass transition. Gutzow and Schmelzer [39] draw an analogy of \( d_i S \simeq 0 \) in slowly varying glasses with Prigogine’s principle of minimum entropy production [11]. However, we will not assume \( d_i S \simeq 0 \) so as to make our argument as general as possible. Later in this work, we will derive an almost identical expression to Eq. (10) as an identity; see Eq. (68). In the conventional view, the entropy of the glass is schematically represented by the short dashed curve in Fig. 3; the upper solid curve represents the entropy of the supercooled liquid (SCL) that would be eventually observed if we wait long enough for the system to equilibrate. The point where \( S_{GL,CV}(T_0) \) branches out of \( S_{SCL}(T_0) \) is the glass transition temperature \( T_{0g} \) and is determined by the choice of observation time \( \tau_{obs} \). As the entropy of the conventional glass lies above the supercooled liquid entropy

\[
S_{GL,CV}(T_0, t) > S_{SCL}(T_0) \quad \text{for} \quad T_0 < T_{0g},
\]

the entropy of the glass actually decreases in time

\[
\frac{dS_{GL,CV}(T_0, t)}{dt} < 0. \tag{13}
\]

The entropy of the conventional glass (blue short dashed curve) approaches \( S_R > 0 \) if we extrapolate to absolute zero for most glasses. In this view, the glass continuously emerges from the supercooled liquid at \( T_{0g} \). Both entropy functions are continuous with only gradual variation determined by their respective heat capacities.

**B. Unconventional Glass View (UV)**

Despite the success of the conventional view that provides a justification of the residual entropy, there have been several attempts to argue that the residual entropy is not a physical concept [34, 38]. It has been suggested that the entropy of a glass should approach 0 at absolute zero, regardless of how it is prepared. In other words, the entropy of a glass has no memory of its mode of preparation at absolute zero, notwithstanding the fact that
The entropy of the supercooled liquid ($S_{\text{SCL}}$: upper solid curve) and of the CV-glass ($S_{\text{GL,CV}}$: short dashed curve) in the conventional view (CV) are shown schematically. We are considering an isobaric cooling experiment. The entropy $S_{\text{GL,CV}}$ of the CV-glass continuously emerges out of $S_{\text{SCL}}$ at $T_{0g}$ and approaches the residual entropy at absolute zero (not shown). Schematic form of the entropy $S_{\text{GL,UV}}$ in the unconventional view (UV) is shown by a discontinuous entropy loss (thin dashed vertical line of magnitude $S_R$) at $T_{0g}$ or a continuous entropy loss (dashed curve) of $S_R$ from $S_{\text{SCL}}$ to the lower solid curve during the glass transition across $T_{0g}$. Note the presence of an inflection point in the dashed piece of $S_{\text{GL,UV}}$; the latter approaches 0 at absolute zero upon extrapolation (not shown). In the presence of an additional variable $\xi$, see text, the entropy curves turn into surfaces defined over the $T_0 - \xi$ plane.

Most glasses do not represent equilibrium states. The total loss of memory of the mode of preparation is the hallmark property of an equilibrium state, while a non-equilibrium state remains strongly correlated with its mode of preparation until it fully equilibrates, which is reflected in its relaxation towards equilibrium. Despite this, the above suggestion has been made repeatedly in the literature. If it is true, it will require either an abrupt or a gradual but rapid reduction in the entropy as the supercooled liquid (SCL) turns into a glass (GL) at (in the former case) or around (in the latter case) $T_{0g}$ as we cool SCL. The amount by which the entropy must decrease during the glass transition (by confinement to one of the possible exponentially large number of components) should be comparable to $S_R$. This is
the unconventional view (UV) described above. The abrupt entropy reduction during the glass transition is shown by the thin vertical dashed line of height $S_R$ at $T_{0g}$ to the lower solid entropy curve of the unconventional glass shown as Glass (UV) in Fig. 3. The gradual entropy reduction is shown by the dashed red portion with an inflection point, which falls very rapidly below the entropy of the supercooled liquid. The total additional entropy reduction is equal to $S_R$. After the drop, the dashed curve connects with the schematic lower solid Glass (UV), which when extrapolated to absolute zero will now give a vanishing entropy, thus resulting in no residual entropy. We note that because of the entropy reduction,

$$S_{GL,UV}(T_0, t) < S_{SCL}(T_0) \text{ for } T_0 < T_{0g},$$

so that the entropy of the glass actually increases in time

$$\frac{dS_{GL,UV}(T_0, t)}{dt} > 0,$$

which is of opposite nature to that in Eq. (13).

C. Gibbs free energy: VConventional versus Unconventional

Thus, it appears that there are two competing views at present as far as the entropy of the glass is concerned with contradicting behavior of the entropy during relaxation as seen from Eqs. (13-14). However, they both accept the same entropy function $S_{SCL}(T_0)$ of the supercooled liquid before it turn into a glass, and is given by the solid blue curve indicated by "Supercooled Liquid." As the enthalpy $H$ and the volume $V$ of the glass are known to be continuous during the glass transition [17-20], both views agree on the same functions $H_{GL}(T_0)$ and $V_{GL}(T_0)$ for the glass. The Gibbs free energy $G(T_0)$ has been identified in I as $G(T_0) \equiv H(T_0) - T_0S(T_0)$ in terms of the entropy of the system. Conversely, the entropy can be obtained from the Gibbs free energy. Then the continuity of the entropy in the conventional view ensures that the Gibbs free energy $G_{GL,CV}(T_0) \equiv H_{GL}(T_0) - T_0S_{GL,CV}(T_0)$ of the glass is also continuous. This is shown by the short dashed piece in Fig. 4 that emerges out of the lower solid curve $G_{SCL}(T_0)$ without any inflection point. In the unconventional view, the Gibbs free energy abruptly jumps upwards by an amount close to $T_gS_R$ for an abrupt reduction of entropy or rises rapidly along the dashed curve with an inflection point to meet continuously with the upper solid curve to give $G_{GL,UV}(T_0) \equiv H_{GL}(T_0) - T_0S_{GL,UV}(T_0)$
FIG. 4: Schematic form of the free energy $G_{\text{SCL}}$ (lower solid curve), $G_{\text{GL,CV}}$ (short dashed curve) and $G_{\text{GL,UV}}$ (vertical jump at $T_{0g}$ or a continuous dashed piece along with the solid upper curve). The dashed piece has an inflection point A, so that it has a region of positive curvature at higher temperatures. There is no inflection point in $G_{\text{GL,CV}}$ and $G_{\text{SCL}}$. In the presence of an additional variable $\xi$, see text, the Gibbs free energy curves turn into surfaces defined over the $T_0 - \xi$ plane.

in Fig. 4 Both Gibbs free energies coincide at absolute zero:

$$G(0) \equiv G_{\text{GL,CV}}(0) \equiv G_{\text{GL,UV}}(0) = H_{\text{GL}}(0),$$

as shown in Fig. 4. Otherwise,

$$G_{\text{GL,CV}}(T_0 > 0) < G_{\text{GL,UV}}(T_0 > 0) \quad \text{for} \quad T_0 < T_{0g}.$$ 

The abrupt entropy reduction in the unconventional view has been recently criticized by Goldstein [41], Gutzow and Schmelzer [39], Nemilov [40], Gujrati [8, 23, 42], and Johari [43]. We will not go into their arguments here for which the reader is advised to go to the original source; however, Johari [43] provides a good summary of these approaches. In addition, Kozliak and Lambert [44] provide a new look at the issue of the residual entropy.
These attempts are different from the approach we take here, although we arrive at a similar conclusion. These previous attempts neither consider a continuous entropy reduction nor do they visit the issue of how to define the entropy for non-equilibrium states from first principles, or how to interpret the residual entropy from a statistical point of view, the issues that guide us here. Therefore, the previous attempts do not reveal a pathological aspect of the continuous entropy reduction in that the behavior of the entropy $S_{GL,UV}(T_0)$ in Fig. 3 is not consistent with the entropy obtained from the Gibbs free energy $G_{GL,UV}(T_0)$ in Fig. 4. This internal inconsistency poses a major problem for the unconventional view.

If the entropy can be defined for a non-equilibrium body from first principles and if it satisfies the second law, then we should be able to test whether component confinement results in an entropy reduction or whether the residual entropy is real for a non-equilibrium body.

III. IMPORTANT CONCEPTS AND USEFUL RESULTS FROM I & II

Quantities pertaining to $\Sigma_0$ are denoted by a subscript 0, for $\Sigma$ without any subscript and for $\tilde{\Sigma}$ by a tilda at the top. The system, although macroscopically large, is considered to be a very small part compared to the medium $\tilde{\Sigma}$, so that the system can only create a very weak disturbance on the medium. As said earlier, a body refers to any of the three systems $\Sigma$, $\tilde{\Sigma}$ and $\Sigma_0$. For the sake of convenience, quantities pertaining to a body will be denoted without any subscript.

A. State variables and internal equilibrium

We first need to clarify the concept of the macroscopic state of a body. As equilibrium and non-equilibrium thermodynamics is an experimental science, it must be based on observables, which we take to be extensive and collectively denote by $X(t)$, $t$ being the time measured from some convenient reference point. Any thermodynamic state function must be a function of state variables $Z(t)$ consisting of observable $X(t)$ and internal variable $I(t)$. The observables are independent continuous variables that can be controlled and manipulated by an observer so that their values will allow the observer to differentiate between different macroscopic states (macrostates) of the same system. Of the observables, the energy $E$, volume $V$ and
the number of particles \( N \) play an important role. The observables are important as they remain fixed for an isolated system. The internal variables (see II for details, where they are denoted collectively by \( \mathbf{I}(t) \equiv \{I_k(t)\} \)) cannot be controlled by the observer, but play a very important role during relaxation in non-equilibrium bodies such as glasses. In addition, the state function may also be an explicit function of time \( t \). It is useful to replace \( \mathbf{I}(t) \) by the dimensionless vector \( \mathbf{\xi}(t) \equiv \{\xi_k(t)\} \) defined according to

\[
\xi_k(t) \equiv \frac{I_k(t) - I_k(\infty)}{I_k(0) - I_k(\infty)}.
\]

The variables \( \xi_k \) are usually known as "internal order parameters" or the "degree of advancement." Being a state function, the entropy of a body, whether in equilibrium or not, is a continuous function of the state variables and will be expressed as \( S(\mathbf{Z}(t), t) \) or \( S(\mathbf{X}(t), \xi(t), t) \).

When the body refers to the isolated system \( \Sigma_0 \), we should remember that its observables are fixed so that \( \mathbf{X}_0 \) has no \( t \)-dependence. The entropy of \( \Sigma_0 \) must be expressed as \( S_0(\mathbf{X}_0, \mathbf{I}_0(t), t) \) or \( S_0(\mathbf{X}_0, \mathbf{\xi}_0(t), t) \) while it is relaxing towards its equilibrium state. Once it reaches equilibrium, its entropy can only be described as a function of its observables, so that it must be expressed as \( S_{0, eq}(\mathbf{X}_0) \), which is now a constant, independent of \( t \). The explicit \( t \)-dependence has disappeared. At the same time, \( \mathbf{\xi}_0(t) \) is also no longer \( t \)-dependent. This means that in equilibrium, \( \mathbf{\xi}_{0, eq} \) must become constant, which from its definition above must vanish identically:

\[
\mathbf{\xi}_{0, eq} \equiv 0. \tag{16}
\]

Moreover, as discussed in II, \( \mathbf{I}_0(t) \) is no longer an independent variable; it becomes a function of the observable \( \mathbf{X}_0 \):

\[
\mathbf{I}_{0, eq} = \mathbf{I}_{0, eq}(\mathbf{X}_0).
\]

For an open system in equilibrium, \( \mathbf{\xi}_{eq} \) also must become constant in equilibrium; similarly, \( \mathbf{I}_{eq} \) is also no longer an independent variable; it becomes a function of the observable \( \mathbf{X}_{eq} \):

\[
\mathbf{\xi}_{eq} \equiv 0, \quad \mathbf{I}_{eq} = \mathbf{I}_{eq}(\mathbf{X}_{eq}).
\]

The case when the entropy of a body has no explicit \( t \)-dependence, so that the entropy appears as

\[
S(\mathbf{X}(t), \mathbf{\xi}(t)), \tag{17}
\]

19
is quite special as discussed in I and II. In this case, the system is said to be in *internal equilibrium*. Accordingly,
\[ \frac{\partial S}{\partial t} = 0 \]  
(18)
under internal equilibrium. The entropy has the maximum possible value for given \( Z(t) \). In this case, the derivatives
\[
y(t) = \frac{Y(t)}{T(t)} = \frac{\partial S(Z(t))}{\partial X(t)}, \quad a(t) = \frac{A(t)}{T(t)} = \frac{\partial S(Z(t))}{\partial I(t)}
\]
(19)
of the entropy with respect to \( Z(t) \) give the field \( Y(t) \) and affinity \( A(t) \) characterizing the body; see II and below. They are defined only when the body is in internal equilibrium or in equilibrium. Otherwise, the derivatives do not have any physical significance.

It will prove useful to think, at least in a formal sense, that the internal variable can also be kept fixed. Consider the system in internal equilibrium at the instance when its state variables are
\[
X_{IE} \equiv X(t), \quad I_{IE} \equiv I(t),
\]
and its field and affinity vectors are
\[
Y_{IE} \equiv Y(t), \quad A_{IE} \equiv A(t).
\]
The medium \( \tilde{\Sigma} \) is characterized by \( Y_0 \), and \( A_0 = 0 \), and will be expressed as \( \tilde{\Sigma}(Y_0, 0) \); see II. We now disconnect this system from the medium and bring it in contact with another medium \( \tilde{\Sigma}(Y_{IE}, A_{IE}) \) that is characterized by \( Y_{IE} \) and \( A_{IE} \). The system is in equilibrium with this medium, with the average values of its observables and internal variables given by \( X_{IE} \) and \( I_{IE} \), respectively. Being in equilibrium, it must satisfy all the requirements of stability. In particular, the heat capacity of the system must be non-negative:
\[
C_{Y_{IE}, A_{IE}} \geq 0, \quad (20)
\]
where \( Y'_{IE} \) represents all fields except \( T_{IE} \). One can also formally consider this equilibrium system as an isolated system with fixed \( X_{IE} \) and \( I_{IE} \) by disconnecting it from the second medium. This isolated system is still in equilibrium, as its entropy is at its maximum for given \( X_{IE} \) and \( I_{IE} \). The heat capacity of such a system should also be non-negative
\[
C_{X_{IE}, I_{IE}} \geq 0, \quad (21)
\]
where $X'_{IE}$ denotes all observables except energy $E(t)$. If we connect this system to a medium which only controls $E_{IS}$ and $V_{IS}$ of the system by its fixed $T_{IE}$ and $P_{IE}$, respectively, with the remaining observables $X''_{IE}$ and $I_{IE}$ kept fixed, then the stability of such a system ensures that the following heat capacity is also non-negative:

$$C_{P_{IE},X''_{IE},I_{IE}} \geq 0.$$  \hspace{1cm} (22)

**B. Gibbs free energy of the system**

From now on, we will considerably simplify our discussion by considering only $E, V$ and $N$ as the only observables of a body, and allow only one internal variable in describing it, which we denote simply by $\xi$. Moreover, we will keep $N$ fixed and allow the possibility of fluctuating $E$ and $V$ due to exchange with another body, the medium. Accordingly, we will not exhibit $N$ in expressing any state function of the body. Thus, $X$ will refer to $E, V$ and $Z$ will refer to $E, V, \xi$ from now on. We also assume that the medium is in internal equilibrium, so that its entropy $\tilde{S}(\tilde{Z})$ does not have an explicit $t$-dependence (so that Eq. \hspace{1cm} (18) is satisfied), although it is not in equilibrium with the system. It follows from the internal equilibrium of $\tilde{\Sigma}$ that the associated fields are

$$\frac{1}{T_0} \equiv \left( \frac{\partial \tilde{S}}{\partial E} \right)_{Z_0}, \quad \frac{P_0}{T_0} \equiv \left( \frac{\partial \tilde{S}}{\partial V} \right)_{Z_0}.$$  \hspace{1cm} (23)

Here, $Z_0$ denotes $E_0, V_0$ and $\xi_0$ of $\Sigma_0$. The affinity $A_{0\xi} = 0$ for the medium. The entropy $S_0(t)$ of $\Sigma_0$ is a continuous function of time $t$, at least twice-differentiable with respect to its extensive variables, and satisfies Eq. \hspace{1cm} (2). As discussed in I and II, it can be written as the sum of the entropies $S(t)$ of the system and $\tilde{S}(t)$ of the medium

$$S_0(E_0, V_0, \xi_0, t) = S(E, V, \xi, t) + \tilde{S}(\tilde{E}, \tilde{V}, \tilde{\xi})$$  \hspace{1cm} (24)

by invoking their quasi-independence. We will provide a direct proof of this sum later in Sect. \hspace{1cm} IV when we identify the entropies as statistical quantities in terms of probabilities of microstates. In terms of

$$H(t) \equiv E(t) + P_0V(t), \quad G(t) \equiv H(t) - T_0S(t) = E(t) - T_0S(t) + P_0V(t),$$  \hspace{1cm} (25)

which are the time-dependent Gibbs free energy and the enthalpy, respectively, of the system $\Sigma$ at fixed $T_0, P_0$ and $A_{0\xi} = 0$, we have

$$S_0(t) - \tilde{S}_0 = S(t) - H(t)/T_0 = -G(t)/T_0,$$  \hspace{1cm} (26)
as shown in I. where $\tilde{S}_0 \equiv \tilde{S}(E_0, V_0, \xi_0)$ is independent of the system.

**Theorem 1** The Gibbs free energy $G(T_0, P_0, t)$ of the system given in Eq. (11) is determined by the temperature and pressure of the medium and is equal to

$$G(T_0, P_0, t) \equiv T_0[\tilde{S}_0 - S_0(t)]. \quad (27)$$

This is an important observation for the following two reasons. Firstly, it shows that the Gibbs free energy is defined even though we may not define the temperature and pressure of the system, a situation that occurs when the system is not even in internal equilibrium. Of course, we are assuming that the energy, volume and entropy of the system are defined under all circumstances. While there is less doubt that this is possible for the mechanical quantities (such as energy and volume), the concept of entropy valid under all conditions requires some care; see I and Sect. IX later. In engineering context, the above Gibbs free energy $G(T_0, P_0, t)$ is also known as *exergy* or *availability* [45].

Secondly, the above conclusion makes an important statement about the *continuity* of $G(t)$, which we now explain. We first recall that the entropy $S_0(t)$ is a continuous function. Now, $\tilde{S}_0$ is the entropy of the medium in internal equilibrium (but at $E_0, V_0, \xi_0$). As said above, the properties of a body in internal equilibrium is similar to those of the same body in equilibrium, when treated as an isolated system. Since the entropy of an isolated system is taken to be continuous, $\tilde{S}_0$ must be continuous. This ensures that the difference $S_0(t) - \tilde{S}_0$ is also continuous, which then proves that $G(T_0, P_0, t)$ is a continuous function.

Since the system is an extremely small part of the isolated system, we have

$$(\frac{\partial S_0}{\partial \xi_0})_{z_0} = (\frac{\partial \tilde{S}}{\partial \xi})_{z_0} = \frac{A_0\xi}{T_0} = 0$$

to a high degree of accuracy. Thus, we have

$$\frac{d}{dt} [S_0(E_0, V_0, \xi_0, t) - \tilde{S}(E_0, V_0, \xi_0)] = \frac{\partial S_0}{\partial t} = \frac{dS_0}{dt} \geq 0,$$

where we have used $A_0\xi = 0$, the constancy of $E_0, V_0$ and the second law. The above equation is valid even if $\xi_0$ is not constant, and immediately proves Eq. (12).

Thus, we come to another very important conclusion, which we state as a theorem:

**Theorem 2** The Gibbs free energy $G(T_0, P_0, t)$ of the system is always a continuous function of time that continuously decreases in time in accordance with Eq. (12).
The above result does not require any knowledge of the state of the system Σ. In particular, the continuity of \( G(t) \) must remain valid even if the processes going on within the system are chemical reactions, ergodicity loss, chaos, turbulence, explosion, etc. or just normal quasi-static slow processes going on in Σ. Thus, the continuity of \( G(t) \) is valid when the system is not in equilibrium with itself or with the medium. As time goes on, \( G(T_0, P_0, t) \) will continue to decrease towards the equilibrium value \( G(T_0, P_0) = E(T_0, P_0) - T_0S(T_0, P_0) + P_0V(T_0, P_0) \).

We now follow its consequences. Let us assume that the system is in equilibrium with the medium at some temperature \( T_1 \) and pressure \( P_1 \) of the latter. The Gibbs free energy of Σ in equilibrium is

\[
G(T_1, P_1) = E(T_1, P_1) - T_1S(T_1, P_1) + P_1V(T_1, P_1);
\]

obviously, equilibrium quantities do not have any explicit \( t \)-dependence. At \( t = 0 \), the system is brought in contact with a medium at the current temperature \( T_0 \) and pressure \( P_0 \). As the energy, entropy and volume have not had any time to change, the new Gibbs free energy at \( t = 0 \) will be

\[
G(T_0, P_0, t = 0) = E(T_1, P_1) - T_0S(T_1, P_1) + P_0V(T_1, P_1).
\]

This is true regardless of what changes may occur at \( t > 0 \). It is clear that the two Gibbs free energies are very different. Their difference is

\[
\Delta G(t = 0) = -S(T_1, P_1)\Delta T + V(T_1, P_1)\Delta P \neq 0, \tag{28}
\]

where \( \Delta q = q_{\text{current}} - q_{\text{prior}} \) for any quantity \( q \). The difference \( \Delta G(t = 0) \) at \( t = 0 \), however, has no physical significance for the second law as the current isolated system with the medium at \( T_0, P_0 \) is different from the previous isolated system with the medium at \( T_1, P_1 \), while the second law refers to the behavior of a body in time under fixed macroscopic conditions. We should also note that \( \Delta G(t = 0) \rightarrow 0 \) as \( \Delta T \) and \( \Delta P \) vanish simultaneously for any system. Thus, if the macroscopic conditions do no change, the Gibbs free energy undergoes no discontinuity at \( t = 0 \).

For \( t \geq 0 \), however, we are observing the same current isolated system, for which Eq. \( \text{(26)} \) holds so that the Gibbs free energy \( G \) of the system must vary continuously for \( t \geq 0 \) regardless of the kinds of processes going on inside \( \Sigma_0 \).
It is interesting to note that for infinitesimal changes in the temperature and pressure, Eq. (28) reduces to
\[ dG(t = 0) = -S(T_1, P_1)dt + V(T_1, P_1)dP, \] (29)
a familiar expression from equilibrium thermodynamics.

If and when the internal equilibrium has been established in \( \Sigma \), we can introduce, as discussed in I, its instantaneous fields and affinities, such as the temperature \( T \equiv T(t) \) and pressure \( P \equiv P(t) \):
\[
\frac{1}{T(t)} = \frac{\partial S}{\partial E}, \quad \frac{P(t)}{T(t)} = \frac{\partial S}{\partial V}, \quad \frac{A_\xi(t)}{T(t)} = \frac{\partial S}{\partial \xi};
\] (30)
see Eq. (19). These are standard relations for the entropy for a body under internal equilibrium and are used commonly in non-equilibrium thermodynamics [1, 2, 8–11]. To ensure that the inequality in Eq. (2) remains valid during relaxation, i.e. during approach to equilibrium, we must have (see also [46])
\[
T(t) \neq T_0, \quad P(t) \neq P_0, \quad A_\xi(t) \neq A_0\xi = 0.
\] (31)
They become identical only when equilibrium has been achieved. Thus, as long as the relaxation is going on due to the absence of equilibrium, the two inequalities must hold true; see I. Thus, we come to another important conclusions:

The use of the internal equilibrium is basically in the spirit of Onsager’s regression hypothesis [47]: Non-equilibrium relaxation is governed by the same laws as the relaxation of spontaneous fluctuations occurring in an equilibrium system.

We will assume that in an isobaric cooling experiment,
\[ P(t) = P_0, \] (32)
which we will refer to as the existence of the mechanical equilibrium for the system. In this case, we find that
\[
\frac{dS_0(t)}{dt} = \left( \frac{1}{T} - \frac{1}{T_0} \right) \frac{dH}{dt} \geq 0.
\] (33)
It can be shown on general grounds (see I) that in a cooling experiment under mechanical equilibrium
\[
\frac{dH}{dt} < 0
\] (34)
during relaxation in glasses. This is also seen experimentally. Thus, in such a cooling experiment

\[ T \geq T_0, \]  

(35)

the equality occurring only when equilibrium has been achieved. Furthermore, in such cooling

\[ \frac{dS}{dt} = \frac{1}{T} \frac{dH}{dt}, \]  

(36)

during relaxation at fixed \( T_0 \). The relaxation that occurs in the glass originates from its tendency to come to thermal equilibrium during which its temperature \( T(t) \) varies with time; recall that we are considering a cooling experiment under mechanical equilibrium. The relaxation process results in the lowering of the corresponding Gibbs free energy, which is a consequence of the second law in Eq. (2) and is valid even when there is no mechanical equilibrium. However, under mechanical equilibrium, the changes in the enthalpy and entropy are in the same direction; see Eq. (36). This then gives rise to the following

**Theorem 3** The lowering of \( G(t) \) with time in an isobaric experiment under mechanical equilibrium results in not only lowering the enthalpy in a cooling experiment, as observed experimentally, but also the entropy \( S(t) \) during relaxation:

\[ \frac{dS}{dt} \leq 0, \]  

(37)

as shown in Fig. 2 for the conventional glass (CV) as it approaches towards the supercooled liquid during relaxation.

**C. Gibbs fundamental relation**

It follows from Eqs. (30) and (18) that

\[ dS(t) = \frac{1}{T(t)} dE(t) + \frac{P(t)}{T(t)} dV(t) + \frac{A_S}{T(t)} d\xi(t). \]  

(38)

This relation is known as the Gibbs fundamental relation. The first law of thermodynamics is codified in the following differential:

\[
\begin{align*}
dE(t) &= T(t)dS(t) - P(t)dV(t) - A_S d\xi_S - A_V d\xi_V - A_\xi d\xi(t) \\
&= T_0 dS(t) - P_0 dV(t) - A_S d\xi_S - A_V d\xi_V - A_\xi d\xi(t),
\end{align*}
\]  

(39) (40)
where the two new and different internal order parameters or degrees of advancement
\[ \xi_S \equiv \frac{S(t) - S(\infty)}{S(0) - S(\infty)}, \quad \xi_V \equiv \frac{V(t) - V(\infty)}{V(0) - V(\infty)}, \]
are determined by the instantaneous entropy and volume governed by their corresponding "affinities"
\[ A_S \equiv -[T(t) - T_0] [S(0) - S(\infty)], \quad A_V \equiv [P(t) - P_0] [V(0) - V(\infty)], \]
thus, \( \xi_S, \xi_V \) play the role similar to that of internal variables \( \xi \), with \( A_S, A_V \) playing the role of their respective affinity. The differential of \( G(t) \) and \( H(t) \), see Eq. (25), turns out to be
\[ dG(t) = -S(t)dT_0 + V(t)dP_0 - A_Sd\xi_S - A_Vd\xi_V - A_{\xi}(t)d\xi(t). \] (41)
and
\[ dH(t) = T_0dS(t) + V(t)dP_0 - A_Sd\xi_S - A_Vd\xi_V - A_{\xi}(t)d\xi(t). \] (42)
For the isobaric case discussed above, we have \( A_V = 0 \), but \( A_S \) is normally non-zero. However, in almost all applications of classical non-equilibrium thermodynamics to glasses to date that we are familiar with, even \( A_S \) is taken to be zero [19, 20]:
\[ A_S = 0. \] (43)
This is equivalent to having
\[ T(t) = T_0, \] (44)
which we will refer to here as the assumption of thermal equilibrium. From Eq. (41), we see that \( G \) cannot vary in time if we have both thermal and mechanical equilibrium and if there are no internal order parameters. Thus, there will be no relaxation unless we allow an order parameter:
\textbf{Theorem 4} Under the assumption of thermal and mechanical equilibrium, internal order parameters are required to describe relaxation observed in glasses.

Except in Sect. [VII], we will not assume mechanical and thermal equilibrium so as to remain as general in our discussion as possible.
IV. NON-EQUILIBRIUM ENTROPY

The results in the previous section are based on the thermodynamic concept of the entropy for a body, not necessarily in equilibrium. Only the difference in the entropy has any meaning as the entropy itself has no unique value, unless supplemented by Nernst postulate [4, 21]. This should be contrasted with the statistical concept of the entropy originally due to Gibbs [3] and based on first principles, which provides a unique value of the entropy for a given macrostate. Everyone believes that the Gibbs entropy is the correct thermodynamic equilibrium entropy [4]. The situation with statistical interpretation of non-equilibrium entropy appearing in Eq. [24] may not be so clear, which we now analyze in this section. The discussion in this section is very general and neither the medium nor the system is assumed to be in internal equilibrium.

A. Fundamental Axiom of Non-equilibrium Thermodynamics

As thermodynamics is an experimental science, it requires several measurements on the body to obtain reliable results. To avoid any influence of the possible changes in the body brought about by measurements, we instead prepare a large number $N$ of samples or replicas under identical macroscopic conditions on which measurements are made. The replicas are otherwise independent of each other in that they evolve independently in time. This is consistent with the requirement that different measurements should not influence each other. The samples are prepared so that the probability of a sample in microstate $j$ is $p_j(Z(t), t)$, which we simply write as $p_j(t)$; it is a continuous function of the state variable $Z(t)$ and of $t$ for a macroscopically large body. We now state the fundamental axiom of thermodynamics as proposed in [8]:

**Fundamental Axiom** The thermodynamic behavior of a system is not the behavior of a single sample, but the average behavior of a large number of independent samples, prepared identically under the same macroscopic conditions at time $t = 0$.

Such an approach is standard in equilibrium statistical mechanics [4, 5, 7, 26], but it must also apply to systems not in equilibrium as it is required for the reliability of measurements. For non-equilibrium systems, this averaging must be carried out by ensuring
that all samples have been prepared with identical history. This is obviously not an issue for systems in equilibrium. We refer the reader to a great discussion about the status of statistical mechanics and its statistical nature in Sect. 25 by Tolman [26]; see also the last paragraph on p. 106 in Jaynes [48]. This point has been recently reviewed in [8, 23].

The average over these samples of some thermodynamic quantity $X$ then determines the thermodynamic average quantity $\overline{X}$ for the body

$$\overline{X}(t) \equiv \sum_{j=1}^{W} p_j(t) X_j,$$  \hspace{1cm} (45)

where $X_j$ is the value of $X$ in the $j$th microstate of the body, and $W$ is the number of its distinct microstates.

**B. General Formulation of Entropy: Isolated system**

1. **Gibbs Formulation of Non-equilibrium entropy**

We begin by considering an isolated system $\Sigma_0$, which need not be in equilibrium. Gibbs [3], Tolman [26] and Rice and Gray [6] among others discuss at length the non-equilibrium entropy using the Gibbs formulation; see also [8, 23]. It is given by the negative average of $\eta \equiv \ln p$,

what Gibbs [3] calls the *index of probability*:

$$S_0(t) \equiv -\overline{\ln p} \equiv -\sum_{\alpha} p_\alpha(t) \ln p_\alpha(t), \quad \sum_{\alpha} p_\alpha(t) = 1,$$  \hspace{1cm} (46)

where $p_\alpha(t)$ is the probability of the $\alpha$th microstate at time $t$. It is shown below that it follows from Eq. (45). As the microstate probability $p_\alpha(t)$ is a continuous function of its arguments $Z_0$ and $t$, the entropy $S_0(t) \equiv S_0(Z_0,t)$ is also a continuous function of its arguments $Z_0$ and $t$. It is straightforward to establish [6, 26] that this entropy satisfies Eq. (2). The identification of the entropy with the negative of the Boltzmann $H$-function [26, see p. 561], the latter describing a non-equilibrium state, should leave no doubt in anyone’s mind that the Gibbs formulation of the entropy can be applied equally well to an equilibrium or a non-equilibrium system in isolation.
For a generic body, we will write the continuous entropy as

\[ S(t) \equiv -\ln p \equiv - \sum_j p_j(t) \ln p_j(t), \quad \sum_j p_j(t) \equiv 1, \]  

(47)

where \( p_j(t) \) is the probability of the \( j \)th microstate of the body at time \( t \). The justification for the entropy expression in Eq. (47) for an open system, its continuity and its connection with the second law will be given below.

There are two different ways to understand the above entropy formulation.

2. Ensemble Interpretation-Dynamics being Irrelevant

We now prove that the entropy is a statistical average given in Eq. (45). We consider a large number \( \mathcal{N} = CW_0(X_0) \) of independent replicas or samples of the isolated system, with \( C \) some large constant integer. Let there be \( \mathcal{N}_\alpha \) samples in the microstate \( \alpha \). The probability of a sample in microstate \( \alpha \) is then

\[ p_\alpha = \frac{\mathcal{N}_\alpha}{\mathcal{N}}. \]  

(48)

The ensemble average of \( Z_0 \) over these samples is given by

\[ Z_0 = \frac{1}{\mathcal{N}} \sum_{\alpha=1}^{\mathcal{N}} \mathcal{N}_\alpha Z_{0\alpha} = \sum_{\alpha=1}^{\mathcal{N}} p_\alpha Z_{0\alpha}, \]  

(49)

where \( Z_{0\alpha} \) is the value of \( Z_0 \) in the microstate \( \alpha \). This is identical to the statistical average given in Eq. (45).

The number of ways \( \mathcal{W} \) to arrange the \( \mathcal{N} \) samples into \( W_0 \) distinct microstates so that there are \( \mathcal{N}_\alpha \) samples in microstate \( \alpha \) is given by

\[ \mathcal{W} \equiv \frac{\mathcal{N}!}{\prod_\alpha \mathcal{N}_\alpha!}. \]

Taking its natural log to obtain an additive quantity

\[ S \equiv \ln \mathcal{W}, \]  

(50)

and using Stirling's approximation for the factorials, we see easily that \( S \) per sample can be written as

\[ \frac{S}{\mathcal{N}} = -\sum_{\alpha=1}^{W_0(X_0)} p_\alpha \ln p_\alpha. \]
where \( p_\alpha \) is given in Eq. (48). Thus, \( S/N \) is the ensemble average of \(-\ln p_\alpha\); thus, it is nothing but the entropy \( S_0 \) of the body given in Eq. (46). Again, the continuity of \( S/N \) follows directly from the continuity of \( p_\alpha \).

The maximum possible value of the entropy for fixed \( X_0 \) is

\[
S_{0,\text{max}}(X_0) = \ln W_0(X_0),
\]

(51)

which occurs if and only if all microstates are *equally probable*:

\[
p_\alpha(t) \to 1/W_0(X_0), \quad \forall \alpha \in \Gamma_0.
\]

This maximum value is the Boltzmann entropy of the system. This certainly occurs as \( t \to \infty \) for most systems. Then the system is said to be in equilibrium. It is evident that the Gibbs formulation in Eq. (46) is more general than the Boltzmann formulation in Eq. (51), as the former contains the latter as a special limit. In equilibrium, \( N_\alpha = C \) for all \( \alpha \), so that \( p_\alpha = 1/W_0 \).

3. Temporal Interpretation-Dynamics being Relevant

Another way to interpret Eq. (46) is as follows, which is quite standard, at least in developing the kinetic theory of gases. We consider the time-evolution of an isolated system \[8, 23\], starting at \( t = 0 \) from some initial microstates \( \alpha_0 \). Then \( p_\alpha(t) \) at some later time \( t \) represents the frequency with which the \( \alpha \)th microstate has occurred during this time interval. This is the temporal definition of the probability \[4\], the traditional way of introducing this probability. All these microstates belong to the slice \( \Gamma_0 \) of the microstate space, consisting of fixed \( X_0 \), but different \( \xi_0(t) \). At \( t = 0 \), \( p_\alpha(0) = \delta_{\alpha,\alpha_0} \), where \( \delta \) is the Kronecker delta, and \( S_0(0) = 0 \). With time, this entropy will continue to increase until it reaches its maximum for fixed \( X_0 \). Let \( W_0(X_0) \) denote the number of distinct microstates in the slice \( \Gamma_0 \).

For whatever reasons, if it happens that the system is confined to, or has visited during certain time interval \( \tau \) (such as the observation time \( \tau_{\text{obs}} \), only a part \( \Gamma_0' \subset \Gamma_0 \) of the above microstate space slice, then

\[
p_\alpha(\tau) = 0, \quad \forall \alpha \notin \Gamma_0',
\]

(52)
even though these microstates corresponds to the same \( X_0 \). This happens because these microstates have not been visited yet. Let \( W_0'(X_0, \tau) < W_0(X_0) \) denote the number of
distinct microstates in $\Gamma'_0$. Then, the conventional entropy in Eq. (46) with the above condition in Eq. (52) would be strictly bounded

$$S_0(X_0, \tau) \equiv -\sum_{\alpha \in \Gamma'_0} p_\alpha(t) \ln p_\alpha(t) \leq \ln W'_0(X_0, \tau);$$

the equality occurs if and only if all these microstates in $\Gamma'_0$ happen to be equally probable:

$$p_\alpha(\tau) = 1/W'_0(X_0, \tau), \quad \forall \alpha \in \Gamma'_0.$$ 

Again we notice the generality of the Gibbs formulation in Eq. (46) over the Boltzmann formulation in Eq. (51).

The ensemble approach is also very important from an experimental point of view. At high temperatures, where dynamics is very fast, it is well known that it agrees with the temporal formulation. However, at low temperatures, where dynamics becomes sluggish as in a glass, the temporal entropy can be misleading. However, the ensemble entropy still gives the correct value. This point has been discussed in [8].

C. General Formulation of Entropy: Open system

Let us now consider our system $\Sigma$ with at least one extensive observable that is fixed [22], which we take to be the number of particles $N$. As usual, the system is a small part of the isolated system $\Sigma_0$. We wish to determine the entropy of $\Sigma$ in terms of its microstates, which are indexed by $i$. Theses microstates correspond to all possible allowed energies and volumes. We use $\tilde{\alpha}$ to denote the microstates of $\tilde{\Sigma}$ with a fixed number of particles $\tilde{N}$. A specification of the microstates $i$ and $\tilde{\alpha}$ gives a unique microstate specification $\alpha$. Hence, the number of microstates $W_0$ of the $\Sigma_0$ is the product $W \tilde{W}$, where $W$ and $\tilde{W}$ are respectively the number of microstates of $\Sigma$ and $\tilde{\Sigma}$. Because of the smallness of $\Sigma$ relative to $\Sigma_0$, which results in the quasi-independence of the system and the medium to a very high degree of accuracy, we have in terms of their probabilities

$$p_\alpha(t) = p_i(t)p_{\tilde{\alpha}}(t).$$

As usual, these probabilities are continuous functions of their arguments. Now, using $\ln p_i(t)p_{\tilde{\alpha}}(t) = \ln p_i(t) + \ln p_{\tilde{\alpha}}(t)$, and the sum rule

$$\sum_{\tilde{\alpha}} p_{\tilde{\alpha}}(t) = 1, \quad \sum_{i} p_i(t) = 1,$$
we find that
\[
S_0(t) \equiv -\sum_i p_i(t) \ln p_i(t) - \sum_\alpha p_\alpha(t) \ln p_\alpha(t),
\]
where the two terms in the above equations represent the entropies of the system and the medium
\[
S(t) = -\sum_i p_i(t) \ln p_i(t), \quad \tilde{S}(t) = -\sum_\alpha p_\alpha(t) \ln p_\alpha(t). \tag{54}
\]
Note that our entire discussion never puts any restriction on the kind of actual processes going on during approach to equilibrium. Hence, whether there is any glass transition, any loss of ergodicity loss, etc., has no bearing on the formulation of entropies in Eq. (54) or our other general results presented in the previous section.

Let us imagine isolating the medium by disconnecting it from the system. Its entropy is given by \(\tilde{S}(t) \equiv \tilde{S}(\tilde{Z}(t), t)\). The isolated medium is similar to the isolated system \(\Sigma_0\), whose entropy was assumed to be continuous; see the discussion immediately after Eq. (2). Thus, \(\tilde{S}(t)\) must also be a continuous function. The continuity of \(S_0(t)\) and of \(\tilde{S}(t)\) then immediately leads to the continuity of the entropy \(S(t)\) of the system. This result is also consistent with the continuity of microstate probabilities \(p_i(t)\). The continuity of \(S(t)\) is independent of the kinds of processes that are going on within it. This discussion then leads us to the following important theorem:

**Theorem 5** The entropy \(S(\tilde{Z}(t), t)\) of an open system is a continuous function of its arguments under all conditions. In particular, it is also continuous when the medium is in internal equilibrium.

The above derivation not only justifies Eq. (11) or Eq. (24) for an isolated system, but also identifies the proper non-equilibrium entropy for our open system \(\Sigma\), which is always a continuous function of its extensive arguments and \(t\). The expression for \(S\) in terms of microstate probabilities in Eq. (54) is identical in form to what one would use for an equilibrium system [4], except that the microstate probabilities are now explicit functions of time \(t\). This entropy then determines the Gibbs free energy and enthalpy in Eq. (25) of the system. The second law in Eq. (2) for the isolated system \(\Sigma_0\) is now expressed in terms of the Gibbs free energy for the system \(\Sigma\) and is given in Eq. (12), provided that the medium is taken to be in internal equilibrium. The fact that \(\Sigma\) is in a medium \(\tilde{\Sigma}\) is reflected in the fact that the \(G(t)\) and \(H(t)\) depend on \(T_0, P_0\) of the medium, and not on \(T(t), P(t)\) and \(A_\xi(t)\)
of the system. Recall that the system may have no well-defined temperature, pressure, etc. unless the system is in internal equilibrium. This is important to emphasize as the validity of the second law cannot depend on the establishment of internal equilibrium in the system. Thus, the entropy formulation in Eq. (54) is very general.

Notice that the ensemble interpretation of the entropy in a body is due to the choice of samples with the probability $p_i$; the *dynamics* within the body never appears in the discussion. Thus, such an interpretation is quite useful when the dynamics in a system becomes very sluggish, such as in a glass.

V. PRINCIPLES OF NON-EQUILIBRIUM THERMODYNAMICS

Based on the discussion above and the Fundamental Axiom, we can formulate four fundamental principles of non-equilibrium thermodynamics [23]. These principles are well known and accepted in equilibrium thermodynamics. We now discuss why they should also be applicable to *slowly* evolving metastable states such as glasses in which we are interested in this work. We will assume that the system of interest is in internal equilibrium, but not in equilibrium with the medium.

1. The first one is the *principle of additivity*, according to which the total entropy or other extensive quantities can be obtained by a sum over different macroscopic parts of the body. Each part must be large enough so that the usual argument that their surface effects can be neglected as thermodynamically unimportant is valid so that the parts become *quasi-independent* [2, 4].

This principle is consistent with what one must do for any measurement, which requires verification by performing the measurement many times over on different samples and performing an average over these samples. Each measurement must be performed under identical macroscopic conditions. We now argue that different quasi-independent parts of the body represent different samples of the body prepared under identical conditions. Consider some body $\Sigma'$ with $N'$ particles, and imagine a much larger body $\Sigma$ that can be divided into a large number of parts $\Sigma'_k, k = 1, 2, \cdots$, each part with $N'$ particles so that they are the same size as the body $\Sigma'$. Let us imagine $\Sigma$ itself to be a very small part of an isolated system $\Sigma_0$, so that various $\Sigma'_k$ and $\Sigma$ do not affect the internal equilibrium of the much
larger medium $\tilde{\Sigma}$. In particular, $T_0, P_0$ and $A_{0\xi} = 0$ of $\tilde{\Sigma}$ are unaffected by $\Sigma'_k$ and $\Sigma$. We can imagine each $\Sigma'_k$ to be in a medium $\tilde{\Sigma}_k$, where the latter is composed of the medium $\tilde{\Sigma}$ and the remainder of the system $\Sigma$ obtained by taking out the part $\Sigma'_k$ under investigation. Because of the smallness of $\Sigma$ relative to $\tilde{\Sigma}$, the new medium also has the same $T_0, P_0$ and $A_{0\xi} = 0$ as the medium $\tilde{\Sigma}$. Thus, each part $\Sigma'_k$ experiences the same $T_0, P_0$ and $A_{0\xi} = 0$ as any other part: all parts experience the same macroscopic conditions. Because of this, different parts $\Sigma'_k$ are nothing but the preparation of the body $\Sigma'$ many times over under identical conditions specified by the same $T_0, P_0$ and $A_{0\xi} = 0$. Thus, averaging any quantity over different samples is equivalent to averaging over different parts $\Sigma'_k$ of $\Sigma$. This principle of additivity must apply to any body even if it is not in equilibrium. Consequently, the value of any extensive quantity over the entire body must be a sum over its various parts, regardless of whether the body is in equilibrium or not.

2. The second principle is the principle of reproducibility, according to which the ensemble average is equal to the average of the experimental values, also called the thermodynamic average.

This principle follows from the Fundamental Axiom according to which thermodynamics, whether equilibrium or time-dependent, requires several measurements on the system to obtain reliable results. To avoid any influence of the possible changes in the system brought about by measurements, we can instead prepare a large number of samples under identical macroscopic conditions. This is consistent with the requirement that different measurements should not influence each other. Then the principle follows immediately from Eq. (49).

3. The third principle is the principle of continuity and uniqueness, which states that the Gibbs free energy is continuous, and hence a unique (single-valued) function of its arguments.

For equilibrium states, this principle is certainly valid. We extend it non-equilibrium systems. The principle follows from Conclusion 2. As said there, its validity is independent of the kinds of processes going on within the system $\Sigma$. In the absence of uniqueness, different experimentalists will have no way to effectively communicate their results and no scientific investigation can be carried out. This is a very important requirement if the second law for an open system in the form of Eq. (12) has to make any sense. The existence of the
Gibbs free energy, as demonstrated in Sect. III B does not require the system be at least in internal equilibrium; it only requires the medium to be in internal equilibrium. Therefore, it is most certainly also valid when the system is in internal equilibrium.

4. The last principle is the principle of stability, according to which the heat capacity, compressibility, etc. must remain non-negative for the system to remain stable.

We have already discussed the non-negativity of the heat capacity in Eqs. (20-22). Similar conditions also apply to compressibility and other response functions.

VI. ENTROPY AS A MACROSTATE PROPERTY AND COMPONENT CONFINEMENT

Can there anything be wrong with the original argument that suggests entropy reduction due to confinement as noted in Sect. II? After all, if the system is confined to just one component, should not the confinement entropy be zero? What can be wrong with such a simple argument? To answer this question, we need to understand the concept of the statistical entropy, to which we now turn. More details can be found in a recent review [8].

A. Non-interacting Ising Spins: Ensemble and Temporal Descriptions

Let us consider an ensemble of $N$ non-interacting Ising spins located at the sites of a lattice with $N$ sites. All possible $W = 2^N$ microstates have the same energy $E = 0$, and each microstate $\mathcal{I}_j$ has the same a priori probability $p_j = 1/W$. The spin macrostate $\mathbf{I}$, on the other hand, is only specified by the number of up and down spins, and not the sequence of spin states on the lattice. One can relate this problem to picking $N$ balls with replacement from an urn containing equal number of balls of two colors. After picking a ball, we must place it back in the urn. The sequence of the colors of the $N$ balls in time with replacement determines a microstate $\mathcal{B}_j$ of the $N$ balls. A ball macrostate $\mathbf{B}$ is determined by specifying only the number of balls of each color, but not the actual sequence of colors. We can identify the state of the $k$th spin in $\mathcal{I}_j$ with the color of the ball picked at the $k$th attempt in $\mathcal{B}_j$. Then the two problems are identical, except that we are considering an ensemble of the Ising spins, whereas we are considering a temporal description for the balls. Indeed, in the latter
case, we have a temporal evolution of the state of a single ball in time. Now, there is no dynamics that allows a ball microstate $B_j$ to change into another ball microstate $B'_j$. There may be some dynamics that could change a spin microstate $I_j$ to another microstate $I'_j$. Whether there is any microscopic dynamics specified or not is irrelevant in determining the entropy for the spins.

The entropy for both systems, spins and balls, is

$$S = N \ln 2.$$ 

It is also the maximum entropy, indicating that we are dealing with an equilibrium state. This entropy will be the same even if there were no dynamics changing the spins, such as at absolute zero in classical mechanics. When a system is confined to one of disjoint components of the phase space from which it cannot escape, we also encounter a situation with the absence of a dynamics, the dynamics which takes the system from one component to another \[8, 12, 23\]. Accordingly, every realization of the balls or spins will remain in its microstate forever, just like a glassy system which remains confined to a disjoint component \[8, 12, 19, 20, 23\] due to kinetic freezing. However, as the Fundamental Axiom states, the entropy is an average quantity obtained by an average over all samples or microstates, as shown in Eq. \[47\]. This is equivalent to saying that the entropy is determined by the macrostate, which represents a collection of microstates, each with certain a priori probability. The entropy has a contribution from all of these microstates. It is not the property of a single microstate. This point should be very clear from the derivation of relating $S/N$ in Eq. \[50\] with the entropy. The evaluation of $S$ is due to the choice of various samples; the dynamics is not part of the derivation. As a consequence, the entropy is unaffected by whether microstates have any dynamics for change or not in time. One only needs to know the probability distribution for the microstates.

For a kinetically frozen glass, different samples will correspond to a glass confined to any one of the components \[8, 12, 23\]. We have no information as to which component a sample is frozen into. Thus, the entropy must be obtained by averaging over these different samples or disjoint components. We cannot just consider one particular sample, since the entropy is not the property of a single component.
B. Probability Collapse and Entropy Reduction

Is it possible to justify that the entropy is determined by considering just one of the components in which the system is confined? If such a determination is possible, it must be because the entropy discontinuously decreases when the component confinement occurs.

The reduction in entropy is most certainly possible if we perform a measurement to identify the microstate in which a given sample is. To identify a particular microstate requires complete information about the body, which is ordinarily unfeasible. In order to identify any particular microstate, we need to perform a very special kind of measurement, which we will call a microstate measurement, that provides us with the complete information about the body in its current microstate $j_0$. For the Ising model, this requires determining the orientations of each of the $N$ spins. After the microstate measurement, we know with certainty which microstate the system is in. Before the measurement, a given sample is known to be in one of the microstates. The probability $p_0$ that the sample is in microstate $j_0$ is $p_0 = 1/W$. This probability changes discontinuously from $p_0 = 1/W$ to $p_0 = 1$ immediately after the measurement. The effect of the microstate measurement is to also reduce the probabilities of all other microstates $j' \neq j_0$ to $p_{j'} = 0$ for this sample. Thus,

$$p_j = \delta_{j,j_0},$$

immediately after the measurement. We will speak of probability collapse to indicate this change in the probability brought about by the microstate measurement in this work. The entropy also vanishes in an abrupt fashion immediately after the measurement from the initial value of $\ln W$ in accordance with complete certainty about the body.

While quite an appealing argument for the justification, it overlooks two important facts:

1. In experimental glass transition, no such measurement is ever made that identifies precisely which component the glass is frozen in. Such a measurement will tell us precisely the positions and momenta of all the $N$ particles which then allows us to decipher which particular component the glass is in.

2. Because of the lack of such a measurement, we must determine the entropy by averaging over all components as shown in Eq. (55) by considering all possible samples with the probability distribution $p_\lambda$ for the components.
C. System Confined in a Component: The Residual Entropy

In real glass formation, no probability collapse occurs as no microstate measurement is ever performed to identify the particular component the sample is in. The sample still has the same probability to be in any of the \( C \) components it had before the confinement occurs. The confinement does not alter the probability distribution. All we know for sure is that a glass sample is in any one of the \( C \) components. We do not know the actual component it is in. This situation is identical to the die which is known to be in one of the six possibilities when it is concealed by the cup, or to the non-interacting Ising spins discussed earlier. As long as the die is concealed, the probability of an outcome of an unloaded die remains \( \frac{1}{6} \), regardless of what is on the top face. Even if the outcome cannot change when we lift the cup, the outcome is most certainly not certain when concealed by the cup; see [8] for more details on this point. The information that the glass has been formed is most certainly not equivalent to knowing precisely the particular component in which the glass is trapped. The latter will require the collapse of the original probability distribution by a microstate measurement. The entropy is obtained by taking the average over all the samples, and not only one glass sample, in accordance with the Fundamental Axiom.

Let us now follow this line of reasoning. The entropy \( S(t) \) can be written as a sum over all the components, indexed by \( \lambda = 1, 2, \ldots, C \)

\[
S(t) = \sum_{\lambda=1}^{C} \sum_{j_\lambda} (-p_{j_\lambda} \ln p_{j_\lambda}), \quad \sum_{\alpha=1}^{C} \sum_{j_\alpha} p_{j_\alpha} = 1,
\]

where \( j_\lambda \) represents one of the microstates in the component \( \lambda \), the first sum is over all the components and the second sum is over all microstates in each component. The above way of writing is an identity and applies under all cases. Thus, it applies whether confinement occurs or not. Introducing

\[
p_\lambda \equiv \sum_{j_\lambda} p_{j_\lambda}, \quad \sum_{\lambda=1}^{C} p_\lambda = 1,
\]

we can rewrite \( S(t) \) as follows:

\[
S(t) = \sum_{\lambda=1}^{C} p_\lambda S_\lambda(t) + S_C(t),
\]

where

\[
S_\lambda(t) \equiv \sum_{j_\lambda} \left( -\frac{p_{j_\lambda}}{p_\lambda} \ln \frac{p_{j_\lambda}}{p_\lambda} \right)
\]
denotes the *component* entropy in a given component $\lambda$, and
\[
S_C(t) \equiv \sum_{\lambda=1}^{C} (-p_\lambda \ln p_\lambda)
\]
denotes the *confinement* entropy due to various components. For an unbiased sampling of the components, $S_C(t)$ must be at its maximum, which requires
\[
p_\lambda = 1/C. \tag{56}
\]
For the case of the die, $S_C = \ln 6$ and $S_\lambda(t) = 0$ to give $S = \ln 6$, as noted earlier.

In real glasses, the entropy $S_\lambda(t)$ vanishes as the glass approaches absolute zero. In this case, the entropy at absolute zero reduces to $S_C(t)$, which is what is customarily called the residual entropy $S_R$ \[19, 20\]. We thus define the residual entropy as
\[
S_R \equiv -\sum_{\lambda=1}^{C} p_\lambda \ln p_\lambda; \tag{57}
\]
when the system explores various components without any bias so that Eq. (56) holds, the residual entropy reduces to
\[
S_R = \ln C. \tag{58}
\]

D. Residual Entropy of Subsystems and Calorimetric Measurements

Another way to understand Eq. (57) is to recall the additive of the entropy. We imagine dividing the system $\Sigma$ into several macroscopically large but equal parts of size $N'$, these parts representing many samples of a smaller system $\Sigma'$. Each part now represents a glass trapped in a component $\lambda'$ of the smaller system $\Sigma'$. Let $C'$ denote the number of disjoint components for $\Sigma'$. Then the number of disjoint components $C$ for $\Sigma$ is given by
\[
C = (C')^{N/N'},
\]
where $N/N'$ denotes the number of $\Sigma'$ parts in $\Sigma$. Again, we cannot be sure of which component $\lambda'$ each part is trapped in. The components appear with probabilities $p_{\lambda'}$ for any part so that
\[
S_R' \equiv \sum_{\lambda'=1}^{C'} (-p_{\lambda'} \ln p_{\lambda'})
\]
for each part. The probability of $\Sigma$ is obtained by adding this entropy over all parts so that

$$S_R \equiv \frac{N}{N'} S'_R.$$ 

If the components appear with no bias, then

$$S_R = \frac{N}{N'} \ln C',$$ 

which coincides with the result in Eq. (58) for $\Sigma$. The additivity principle clearly shows that the residual entropy for $\Sigma$ is not zero.

It is evident now that to conclude that the residual entropy has vanished just because a sample has frozen into a single basin or glass form is incorrect. The entropy reduction for $\Sigma$ only happens if a microstate measurement is performed to identify the particular component the $\Sigma$-glass is in. This discussion also shows that calorimetric measurements explore different glass components associated with the subsystems, so that they reveal a non-zero residual entropy.

E. Spontaneous Symmetry Breaking versus Glass Confinement

It is relevant at this point to contrast the above component confinement in glasses with the idea of confinement that occurs in spontaneous symmetry breaking such as a ferromagnet. In the latter case, there exists a symmetry breaking field, whose presence picks out one of the components, for example $\lambda = \lambda_0$, for the system. This is equivalent to our notion of the microstate measurement, except that in this case it is really a "component measurement" resulting in picking the component $\lambda_0$: the application of the symmetry breaking field forces the system to be in a particular component $\lambda_0$. In this process, the entropy of the system will be reduced by $S_C$ (note that we have suppressed the time-dependence as one usually considers equilibrium situations in symmetry-breaking) due to the probability collapse discussed above on p. 37 and all thermodynamic averages are determined by the particular component $\lambda_0$. It usually happens that the value of $S_C$ in spontaneous symmetry breaking is not an extensive quantity, so the effects of the confinement on the entropy become irrelevant for a macroscopic system. There is no entropy reduction per unit volume in the process of confinement. However, the effects of the confinement on some thermodynamic quantities, such as the order parameter associated with the symmetry breaking, become very important.
For glasses, the residual entropy $S_C(t)$ is found to be an extensive quantity. Therefore, it is very important to know if there could be some entropy reduction due to confinement in glasses. To this date, no one has identified any physical symmetry breaking field analog for glasses. Thus, there does not seem to be a way to prepare a glass in a particular component. When a glass is prepared, we have no way of knowing which component it is trapped in. Hence, one must consider all the components in obtaining any thermodynamic average, such as the entropy as we have done above. In particular, there is no entropy reduction per unit volume in a glass transition.

We have discussed the unsuitability of time-average (instead of the ensemble average) elsewhere [8], and we refer the reader to this for more details. We will only make the following brief comment here. It happens that at low temperatures the approach to equilibrium takes more time than feasible due to experimental constrained. Most measurements last a short period of time. The temporal average over an extended time period has nothing to do with information obtained in measurements that may take a fraction of a second or so. Unless the system is already in equilibrium at the time of the measurement, different measurements carried out on the system at different instances will give different results; the system has a memory effect, when the system is not in equilibrium. Thus, temporal average is not desirable for glasses.

In contrast, the ensemble average provides an instantaneous average and thus bypasses the above objection of the finite measurement time.

**F. Role of Irreversibility on the Residual Entropy**

There is another way to understand the inequalities in Eq. (6). In a vitrification experiment from a state A at temperature $T_0$ in the supercooled liquid state which is still higher than the glass transition temperature to the state $A_0$ at absolute zero, we have along the path $A \rightarrow A_0$

$$S(0) = S(T_0) + \int_A^{A_0} d_e S + \int_A^{A_0} d_i S,$$

(60)

where we have set $\Delta S_C = 0$ as there is no latent heat in the vitrification process, and where $dS = d_e S + d_i S \geq 0$, with $d_i S \geq 0$ representing the irreversible entropy generation and $d_e S = C_P dT_0/T_0$; see Eq. (3). Since the second integral in the above equation is always
non-negative, we obtain

\[ S(0) \geq S_{\text{expt}}(0) \equiv S(T_0) + \int_0^{T_0} C_P dT_0 / T_0, \]

(61)
in accordance with Eq. (6), as expected. The forward inequality is due to the irreversible entropy generation. Thus, the entropy at absolute zero must be larger than or equal to the right hand side \( S_{\text{expt}}(0) \), which can be determined by performing a cooling experiment. We take \( T_0 \) to be the melting temperature \( T_M \), and uniquely determine the entropy of the supercooled liquid at \( T_{0M} \) by adding the entropy of melting to the crystal entropy \( S_{\text{CR}}(T_{0M}) \) at \( T_{0M} \). The latter is obtained in a unique manner by integration along a reversible path from \( T_0 = 0 \) to \( T_0 = T_{0M} \):

\[ S_{\text{CR}}(T_M) = S_{\text{CR}}(0) + \int_0^{T_M} C_{P,CR} dT_0 / T_0, \]

here, \( S_{\text{CR}}(0) \) is the entropy of the crystal at absolute zero, which is traditionally taken to be zero, and \( C_{P,CR}(T_0) \) is the heat capacity of the crystal. This then uniquely determines the entropy of the liquid to be used in the right hand side in Eq. (61). If experiments show that \( S_{\text{expt}}(0) \) greater than zero (or greater than \( S_{\text{CR}}(0) \) if the latter is not taken to be zero in accordance with Nernst postulate), then the entropy \( S(0) \) at absolute zero on the left side itself must be greater than zero (or greater than \( S_{\text{CR}}(0) \)). We will assume that \( S_{\text{CR}}(0) = 0 \). Thus, the experimental determination of the right hand side of Eq. (61) is sufficient to unequivocally determine whether \( S(0) \geq S_{\text{expt}}(0) \). The inequality in Eq. (61) takes into account any irreversibility during vitrification. As is well known, \( S_{\text{expt}}(0) \) is found to be non-negative, as discussed in Sect. I A. Thus, there cannot be any doubt that

\[ S_R \equiv S(0) \geq S_{\text{expt}}(0); \]

(62)
experiments invariably give a non-zero value of \( S_{\text{expt}}(0) \), which then proves immediately that in these cases, the residual entropy cannot vanish.

VII. NON-EQUILIBRIUM ENTROPY AND GIBBS FREE ENERGY

A. Consequences of the Second Law

The important conclusions from the previous discussion can now be summarized as follows. The conclusions are derived under the assumption that the entropy \( S_0 \) of the isolated system is a continuous function of \( E_0, V_0, N_0, \xi_0(t) \) and \( t \).
(A) Medium under internal equilibrium

1. The Gibbs free energy \( G \) of the system is continuous function of its arguments and decreases continuously during relaxation toward its equilibrium value.

2. The entropy \( S \) of the system is continuous function of \( E(t), V(t), \xi(t) \) and \( t \), which follows from Theorem 5.

(B) Medium and system under internal equilibrium

1. The entropy \( S \) of the system is continuous function of \( E(t), V(t), \xi(t) \). This is a weaker form of the continuity condition, and follows from the continuity of the Gibbs free energy in Theorem 2. To see that we write

\[
S = \left( H - G \right)/T_0,  \tag{63}
\]

and use the experimentally observed continuity of \( H \) during the glass transition.

2. The entropy continuously decreases during relaxation toward its equilibrium value according to Eq. (37).

It follows from either (A2) or (B1) that the entropy cannot undergo any discontinuity at a glass transition. Since the continuity of \( G \) follows from the second law, any discontinuous entropy reduction will result in the violation of the second law, a point already made by Goldstein [41].

It follows from (B2) that the behavior of entropy during relaxation only supports Eq. (13) and not Eq. (14). In other words, only the conventional view of the entropy during component confinement can be substantiated by the second law. However, this does not prove that the Gibbs free energy \( G_{GL,UV}(T_0) \) is incorrect as its variation in time conforms to the expected variation in Eq. (12). The Gibbs free energy \( G_{GL,CV}(T_0) \) also conforms to the expected variation in Eq. (12). Does it mean that \( G_{GL,UV}(T_0) \) is just as acceptable as \( G_{GL,CV}(T_0) \) from the point of view of the second law and non-equilibrium thermodynamics, even if \( S_{GL,UV}(T_0) \) is not? Or is it possible that both Gibbs free energies are unacceptable? Then what should be the correct form of the Gibbs free energy for a glass? Is it possible that \( G_{GL,UV}(T_0) \) is acceptable, even though \( S_{GL,UV}(T_0) \) is found to violate the second law? Will this lead to some thermodynamic inconsistent in some way? Is it possible that only \( G_{GL,CV}(T_0) \) is acceptable? We turn to this issue now.
B. Non-equilibrium Entropy evaluation

The Gibbs free energy $G_{GL, CV}(T_0)$ is shown by the short dashed blue curve which gradually connects without any inflection point to $G_{SCL}(T_0)$, while $G_{GL, UV}(T_0)$ is shown by the solid red curve and by its discontinuous or rapid fall to $G_{SCL}(T_0)$ in Fig. 4; the latter possesses an inflection point A in the dashed red portion. We rule out the discontinuous jump in $G_{GL, UV}(T_0)$ as physically unacceptable because of (A1). Thus, we only consider $G_{GL, UV}(T_0)$ with a continuous fall to $G_{SCL}(T_0)$.

All known analyses of experimental data have been carried out under the assumption of mechanical and thermal equilibrium. Therefore, we will also make this common assumption in this section, according to which

$$A_S = A_V = 0.$$  \hspace{1cm} (64)

Accordingly, we will assume that the instantaneous temperature and pressure $T(t), P(t)$ of the system are no different from the constant temperature and pressure $T_0, P_0$ of the medium. As there is no longer any need to distinguish the two, we will use the common notation $T, P$ for both, with the implicit assumption that they have no longer any $t$-dependence.

In our discussion below, we do not specifically endorse the statistical formulation of the entropy in Eq. (54). We simply use the thermodynamic notion of the entropy. The resulting differential of the Gibbs free energy is now given by

$$dG = -SdT + VdP - A_\xi d\xi.$$  \hspace{1cm} (65)

The irreversible entropy generation is captured by the presence of $\xi$ in the above equation. This form of $dG$ is exactly what is postulated in the traditional non-equilibrium thermodynamics \cite{9-11}, where the existence of non-equilibrium entropy is postulated. How it is actually calculated is irrelevant for the general argument below. This point should not be forgotten in the following discussion as the general conclusions should be confirmed by any formulation of the entropy.

The entropy is given by

$$S \equiv -(\partial G/\partial T)_{P, \xi},$$  \hspace{1cm} (66)

which generalizes the conventional definition of the entropy for an equilibrium system to a non-equilibrium system. The above relation shows that we should be able to extract the
entropy $S$ from the knowledge of the Gibbs free energy $G$. Now, it is easy to show that the heat capacity is given by

$$C_{P,\xi}(T) = T \left( \frac{\partial S}{\partial T} \right)_{P,\xi} = -T \left( \frac{\partial^2 G}{\partial T^2} \right)_{P,\xi} \geq 0;$$  \hspace{1cm} (67)

this is in accordance with Eq. (22). We can now integrate Eq. (67) to obtain the entropy in terms of the heat capacity $C_{P,\xi}$:

$$S(T, \xi) = S(0, \xi) + \int_0^T C_{P,\xi}(T) dT + \Delta S_C,$$  \hspace{1cm} (68)

where $S(0, \xi)$ is the residual entropy at absolute zero, and where

$$dQ_{P,\xi} \equiv C_{P,\xi}(T) dT$$

represents the amount of heat at constant $P, \xi$. The Eq. (68) should be compared with Eq. (10), which is usually criticized as unreliable due to the glass transition. In contrast, Eq. (68) is an identity in our non-equilibrium thermodynamics under the assumption in Eq. (64). Any irreversibility in the system is now captured by the time dependence of $\xi$. However, the actual form of the variation is not relevant for our discussion in this work. The integration in this identity must be carried out along constant $\xi$. This heat capacity cannot vanish at any positive temperature. It can vanish at absolute zero without creating any conceptual problem. We have discussed these issues elsewhere. Any state with a negative heat capacity will be identified here as unphysical.

C. Consequences of $\xi$ for Glasses

Let us try to understand the consequence of the additional variable $\xi$. In the presence of $\xi$, all the curves including the broken red curve in Figs. 3 and 4 turn into surfaces defined over the $T-\xi$ plane. In particular, the inflection point A that is present in the dashed piece in this figure turns into a line $A(\xi)$ of inflection points. Thus, if we consider a slice of these surfaces at a constant $\xi = \xi_C$, then this slice will give three curves similar to those shown in Figs. 3 and 4 with $S_{GL,UV}(T_0)$ and $G_{GL,UV}(T_0)$ still containing inflection points. In particular, we will find a region curving down at higher temperatures and a region curving up at lower temperatures in Fig. 3 just as we see in the figure for $S_{GL,UV}(T_0)$. Nevertheless,
the form of the entropy $S_{GL,CV}(T_0)$ or $S_{GL,UV}(T_0)$ for fixed $\xi = \xi_C$ is monotonic as shown in Fig. 3, so that

$$\left( \frac{\partial S}{\partial T} \right)_{P,\xi} = \frac{C_{P,\xi}(T)}{T} > 0 \quad (69)$$

for both of them. Since we are allowed to take any value $\xi_C$ in the above discussion, there is no harm in showing the fixed value as a general $\xi$ in the above equation. The above inequality corresponds to $C_{P,\xi} > 0$, in accordance with Eq. (67). Again, we show $\xi$ and not $\xi_C$ for the reasons alluded to above. In an isobaric experiment at fixed $P$, the curves shown in Fig. 3 need not correspond to a fixed $\xi$ in the glass transition region. In general, we expect $\xi$ to vary with the temperature, pressure and the history of cooling. But the point to stress is that the presence of the inflection point A in Fig. 3 has no effect on the sign of the slope $(\partial S/\partial T)_{P,\xi}$. It remains non-negative for both entropies $S_{GL,CV}(T_0)$ or $S_{GL,UV}(T_0)$.

D. Forms of Gibbs Free Energies

The enthalpy $H_{GL}(T, \xi)$ is the same in both views

$$H_{GL,CV}(T, \xi) \equiv H_{GL,UV}(T, \xi) = H_{GL}(T, \xi),$$

because of the continuity of the enthalpy during the glass transition. The Gibbs free energy

$$G_{GL}(T, \xi) \equiv H_{GL}(T, \xi) - T S_{GL}(T, \xi)$$

thus, has the same value $H_{GL}(0, \xi)$ in CV and UV at absolute zero:

$$G_{GL}(0, \xi) = G_{GL,CV}(0, \xi) \equiv G_{GL,UV}(0, \xi) \equiv H_{GL}(0, \xi),$$

regardless of the value $S_{GL,CV}(0, \xi)$ and $S_{GL,UV}(0, \xi)$ take at absolute zero (we obviously do not consider the unphysical case of an infinitely large $S(T, \xi)$ for a finite but macroscopically large system), depending on whether we follow CV or UV. This is the same as Eq. (15). The SCL Gibbs free energy $G_{SCL}(T)$ above $T_g \equiv T_{0g}$ is the same in both views. If it is possible for the ”Supercooled Liquid” curve to be extrapolated to absolute zero, as shown by the solid blue curve in Fig. 4, then $G_{SCL}(T)$ would have the value $G_{SCL}(0) = H_{SCL}(0) \leq H_{GL}(0, \xi)$ there. Observe that

$$G_{SCL}(T) < G_{GL,CV}(T, \xi) < G_{GL,UV}(T, \xi)$$
for $T < T_g$. The value $G_{SCL}(0)$ should be strictly lower than $G_{GL}(0, \xi)$, as $G_{GL,CV}(T, \xi)$ or $G_{GL,UV}(T, \xi)$ is expected to reach $G_{SCL}(T)$ from above during relaxation. The curve $G_{SLC}(T)$ presumably approaches absolute zero with a slope equal to zero ($S_{SCL}(0) = 0$). The entire supercooled liquid curve $G_{SLC}(T)$ is concave, as shown because it represents a stable state.

E. Constant internal order parameter

Let us first consider the additional variable $\xi$ to be constant for the sake of simplicity of the discussion. Therefore, we will suppress $\xi$ in this section. At absolute zero, the Gibbs free energy in either view takes the same value $G_{GL}(0)$, as noted above; see the solid red curve and the dashed blue curve in Fig. 4. Thus, there are two possible Gibbs free energy curves below the glass transition at $T_g$: $G_{GL,UV}(T)$ or $G_{GL,CV}(T)$. Since the entropy $S$ is given by Eq. (66), it is evident that the magnitude of the slope of $G_{GL,UV}(T)$ will be smaller ($\simeq 0$) than that of $G_{GL,CV}(T)$ near absolute zero because of the entropy reduction, as shown schematically. With no entropy reduction, $G_{GL,CV}(T)$ will have a large, negative slope equal to $-S_R$ at absolute zero. Hence it will drop faster than the upper red curve, so that $G_{GL,CV}(T)$ will be given by the short dashed blue curve in Fig. 4. This curve will eventually connect to the lower solid blue curve $G_{SLC}(T)$ indicated by ”Supercooled Liquid.” The combined curve (short dashed blue curve $G_{GL,CV}(T)$ below $T_g$ and solid blue curve $G_{SLC}(T)$ above $T_g$) remain concave at all temperatures, as shown schematically in the figure, as there is no inflection point. The Gibbs free energy $G_{GL,UV}(T)$ must also be continuously connected with $G_{SLC}(T)$ along the long dashed red curve as shown in Fig. 4; now the connection give rise to an inflection point A.

According to Eq. (67), the Gibbs free energy must be a concave function of the temperature so that the heat capacity remains non-negative, as the solid red curve, the short dashed and solid blue curves in Fig. 4 are. Remember that we are talking about the total heat capacity of the system. It is clear that being concave, $G_{GL,CV}(T)$ gives a non-negative heat capacity. On the other hand, this is not true of $G_{GL,UV}(T)$, which contains an inflection point at $A$ near $T_g$. It is clear that any attempt to smoothly connect the solid red piece $G_{GL,UV}(T)$ with $G_{SLC}(T)$ must result in an inflection, so that it cannot remain concave everywhere. It must have a convex piece giving a negative heat capacity at higher temperatures, as shown by the arrow. Let us emphasize that to connect the two solid curves by a straight piece
to avoid the convex piece is contrary to physics. This will result in a discontinuity in the entropy and, hence, a latent heat where the connection is made. This is contrary to all experimental evidence. In addition, over this intermediate temperature range, the heat capacity will turn out to be zero, which is also contrary to all experimental evidence. Thus, the dashed piece must not be straight for a physically realizable glass.

F. Variable Internal order parameter

Let us now understand the significance of Eq. (67) when a variable internal order parameter \( \xi \) is present. In this case, these free energy curves will turn into surfaces defined over the \( T_0 - \xi \) plane. In particular, the inflection point A in this figure turns into a line of inflection point, as is also the case with Fig. 3. Let us consider a slice of these surfaces obtained by fixing \( \xi = \xi_0 \). As this slice will also cut the line of inflection points, the slice will have the middle piece in which the curvature will change sign on either side of this inflection point. Thus, this slice will appear similar to the curves in Fig. 4 with the middle dashed red curve containing an inflection point at \( T = T_A \). At temperatures lower than \( T_A \), the Gibbs free energy is concave so that Eq. (67) is satisfied. However, at temperatures higher than \( T_A \), the Gibbs free energy becomes convex so that Eq. (67) is not satisfied. This region then results in a region of negative heat capacity, and this makes the system unphysical over this region above \( T_{0A} \). Indeed, all experimental evidence collected so far for glasses have never ever exhibited a negative heat capacity.

The presence of a point of inflexion at \( T_A \), where the heat capacity will vanish, raises another issue. It is obvious that \( T_A \) is a positive temperature. This gives rise to another unphysical aspect of UV in that the glass at this temperature can be brought in thermal equilibrium with any medium at any temperature. No heat exchange is possible \( (dQ_{P,\xi} \equiv C_{P,\xi}dT = 0) \) as the system has vanishing heat capacity. This means that at A where the heat capacity is zero, the temperature has no physical significance for a glass; see the discussion above.

In addition to these problem, the negative heat capacity is in contradiction with (69). The negative curvature of the Gibbs free energy \( G_{GL,UV}(T) \) implies that the entropy must be a decreasing function of the temperature, in direct contradiction with the behavior of the entropy \( S_{GL,UV}(T) \) in Fig. 3. The entropy derived from \( G_{GL,UV}(T) \) is different from the...
entropy $S_{GLUV}(T)$ in Fig. 3. Thus, there is an *internal inconsistency*, a thermodynamic inconsistency, within the unconventional view. The lack of thermodynamic consistency and the violation of Eq. (67) rules out the unconventional view as physically relevant. Only the conventional view can be supported by the second law.

VIII. CONCLUSIONS

The formulation of the second law of thermodynamics in Eq. (2) presupposes the existence and continuity of the entropy $S_0$ of an isolated system under all possible conditions, and not only when the system is in equilibrium. This point is, however, not always appreciated. A microstate is identified by specifying some extensive mechanical quantities of the system such as energy, volume, etc. that we have identified here as state variables denoted collectively by $Z(t)$. These variables, and therefore the microstates and their probabilities $p_i(t)$ exists even if the fields like the temperature, pressure etc. may not exist for the system. As the entropy is a state function, the entropy $S_0$ as identified in Eq. (46) exists for an isolated body under all conditions, and we have assumed it to be a continuous function of $Z_0$ ant $t$. This assumption must be made for Eq. (2) to have any content. We start from this and show that this results in the continuity of the Gibbs free energy in Eq. (25) for an open system; see Theorem 2. The Gibbs free energy exists under all possible conditions of the system. In terms of the Gibbs free energy, the second law for an open body is given by Eq. (12).

If we now assume the open system to be in internal equilibrium, we can identify its fields and affinities by Eq. (19). For a body under internal equilibrium, certain results have been obtained in Sect. III, the most important being Eq. (34) and Eq. (37) under cooling when we have mechanical equilibrium ($P = P_0$). The last observation is later used to rule out any theory of vitrification (via cooling) that predicts an increase of entropy during relaxation. The statistical concept of entropy is introduced in Sect. IV given by Gibbs [3] for an isolated system under all conditions. It follows form the FUNDAMENTAL AXIOM in this section. Under the assumption of quasi-independence, the entropy of an open system follows from this statistical formulation and is given in Eq. (54).

The principles of non-equilibrium thermodynamics are enunciated in Sect. V which follow from the FUNDAMENTAL AXIOM. These principles reduce to accepted principles
of equilibrium thermodynamics. Using these principles, we explain how the entropy of a system should remain continuous during component confinement at a glass transition. We then prove the continuity of $S$ under two distinct situations; see (A2) and (B1). This continuity of $S$ is one of the most important results of this work and is derived under the most possible general condition; see Theorem 5. The statistical entropy merely explains how this happens. The next most important result is captured by Theorem 3 according to which only Eq. (13) can be justified by the second law; Eq (14) cannot be justified. The discussion also explains the concept of the residual entropy. The residual entropy is estimated by the experimentally obtained value $S_{\text{expt}}(0)$ of the entropy, see Eq. (61), by applying equilibrium thermodynamics to the glass, a standard practice in the field. The experimental estimate $S_{\text{expt}}(0)$ is normally a non-negative value. We give a direct proof that the residual entropy must be bounded from below by this experimental value, see Eq. (62), thus making the residual entropy at least as big as the experimental estimate. Any irreversibility will only raise the value of the residual entropy even higher than the experimental estimate. It is impossible for the residual entropy to be zero if the experimental estimate $S_{\text{expt}}(0)$ is non-zero. This conclusion justifies a non-zero $S_R$ at $G$ in Fig. 2.

Using general arguments of stability and well-established non-equilibrium thermodynamics, we have also shown that $G_{\text{GL,UV}}(T)$ is internally inconsistent in Sect. VII D. This conclusion is not based on any particular formulation of the entropy. It only uses the thermodynamic concept of entropy. Our conclusion then adds another argument in support of the reality of the residual entropy. Any entropy reduction scenario during component confinement violates the second law and results in an internal inconsistency.

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