Is Structural Relaxation During Vitrification the Inverse of the Glass Transition?

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Abstract

We have recently applied the second law to an isolated system, consisting of a system Σ such as a glass surrounded by an extremely large medium \( \tilde{\Sigma} \), to show that the instantaneous absolute temperature \( T(t) \), thermodynamic entropy \( S(T_0, t) \) and enthalpy \( H(T_0, t) \) of Σ decrease in any isothermal relaxation towards their respective equilibrium values \( T_0, S_{eq}(T_0) \) and \( H_{eq}(T_0) \) under isobaric cooling. The decrease of the thermodynamic entropy and enthalpy during relaxation in vitrification is consistent with non-negative temperature \( T(t) \). The Gibbs statistical entropy also conforms to the above relaxation behavior in a glass, which however is contrary to the conjecture by Gupta, Mauro and coworkers that the glass transition and the structural relaxation during vitrification are inverse to each other; this is then supported by computation in which their statistical entropy \( \hat{S}(T_0, t) \) drops below \( S_{eq}(T_0) \) during the glass transition and then increases towards it during isothermal relaxation. However, they do not establish that the entropy loss during the glass transition is accompanied by a concomitant entropy gain of the medium to maintain the second law. These authors use a novel statistical formulation \( \hat{S}(T_0, t) \) of entropy based on several conjectures such as it being zero for a microstate, but do not compare its behavior with the thermodynamic entropy \( S(T_0, t) \). The formulation is designed to show the entropy loss. Its subsequent rise not only contradicts our result but also implies that the glass during relaxation must have a negative absolute temperature. To understand these puzzling results and the above conjecture, we have carried out a critical evaluation of their unconventional approach. We find that the inverse conjecture is neither supported by their approach nor by the second law. The zero-entropy microstate conjecture is only consistent with \( \hat{S}(T_0, t) \equiv 0 \) at all temperatures, not just at absolute zero and is found to have no scientific merit. We show that the maximum entropy gain of the medium during the glass transition invalidates the entropy loss conjecture. After pointing out other misleading, confusing and highly exaggerated statements in their work, we finally conclude that their unconventional statistical approach and computational scheme are not appropriate for glasses.

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I. INTRODUCTION

A. Conventional Approach (CA) to Glass Transition

In a recent paper [1], we have studied a homogeneous non-equilibrium system $\Sigma$ surrounded by an extremely large medium $\tilde{\Sigma}$. The work has been extended to also cover inhomogeneous systems and internal variables [2]. The combined system $\Sigma_0$ forms an isolated system; see Fig. 1. We apply the second law to the isolated system to describe the behavior of the non-equilibrium system $\Sigma$. According to the second law [3]

$$\frac{dS_0(t)}{dt} = \frac{dS(t)}{dt} + \frac{d\tilde{S}(t)}{dt} \geq 0,$$

where $S_0(t), S(t)$ and $\tilde{S}(t)$ denote the entropy of $\Sigma_0, \Sigma$ and $\tilde{\Sigma}$, respectively, at time $t$. In this work, quantities pertaining to $\Sigma_0$ have the suffix 0, the system $\Sigma$ have no suffix, and $\tilde{\Sigma}$ have a tilde. For $\Sigma_0$, all of its (additive) observables, variables that can be controlled by the observer, such as its energy $E_0$, volume $V_0$, number of particles $N_0$, etc. are constant in time. These observables also identify the macrostate of $\Sigma_0$. It is clear that for some homogeneous $\Sigma_0$, the variation of its instantaneous entropy $S_0(t)$ cannot be explained by the dependence of the latter on its constant observables. The variation can only be explained by assuming the dependence of $S_0(t)$ on (additive) internal variables, variables that cannot be controlled by the observer, that vary in time as $S_0(t)$ approaches its maximum value. For an inhomogeneous $\Sigma_0$, the variation of its entropy $S_0(t)$ can be explained by the way the inhomogeneity disappears [2] as it approaches equilibrium. The inhomogeneity gives rise to induced internal variables; see below. One may not require any additional internal variable. Thus, if we consider $\Sigma_0$ to consist of $\Sigma$ and $\tilde{\Sigma}$, as we do in this work, it is no longer a homogeneous system as long as $\Sigma$ is not in equilibrium with the medium $\tilde{\Sigma}$. Thus, it is possible to consider $\Sigma_0$ without any internal variable, as was the case studied in [1]. We discover that the instantaneous values of its fields (temperature $T(t)$, pressure $P(t)$, etc.) are in general different from those of the medium ($T_0, P_0$, etc.); see also Bouchbinder and Langer [4]. But the most surprising result of the mathematical analysis is that the instantaneous conjugate variables, the entropy $S(t)$, the volume $V(t)$, etc. play the role of inhomogeneity-induced internal variables with the corresponding ”affinity” [1, 2, 5–8], respectively, related to the deviation $T(t) - T_0, P(t) - P_0$, etc; see Eqs. (14) and (15).

As a non-equilibrium system at fixed $T_0, P_0$ of the medium strives to come to equilibrium,
FIG. 1: Schematic representation of a macroscopically large system \( \Sigma \) and an extremely large medium \( \tilde{\Sigma} \) surrounding it to form an isolated system \( \Sigma_0 \). The system is a very small part of \( \Sigma_0 \). The medium is described by its fixed fields \( T_0, P_0 \), etc. while the system, when it is in internal equilibrium (see text) is characterized by \( T(t), P(t) \), etc.

It undergoes relaxation during which its instantaneous fields \( T(t), P(t) \), etc. continue to change. At the completion of relaxation, the "affinities" vanish so that

\[
T(t) \rightarrow T_0, \quad P(t) \rightarrow P_0, \quad \text{etc.}
\]

as expected. In an isobaric process, which is of central interest to us here, we will assume that the system is always in mechanical equilibrium so that its pressure \( P(t) \) is always equal to \( P_0 \) at all temperatures and all times; however, there is normally no thermal equilibrium so that the instantaneous temperature \( T(t) \) of the system is different from \( T_0 \) \[1, 2, 4\]. It is found that during relaxation, the instantaneous entropy \( S(t) \) of the system continues to decrease in an isobaric cooling experiment such as vitrification. The entropy of Glass1, see Fig. 2 approaches (see the downward arrows) that of the equilibrated supercooled liquid entropy \( S_{eq} \) (shown by the solid curve) from above during relaxation

\[
S(T_0, P_0, t) \xrightarrow{CA} S_{eq}^+(T_0, P_0),
\]

where we have also exhibited the temperature of the medium; being in equilibrium (we do not consider possible crystallization here), the supercooled liquid cannot have any relaxation. It will be our practice to not exhibit \( T_0, P_0 \), unless clarity is needeed, in which case we will
FIG. 2: Schematic behavior of the entropy of the equilibrated supercooled liquid ($S_{eq}(T_0)$: solid curve) and two possible glasses ($S(T_0, t)$: Glass1-dotted curve, $\hat{S}(T_0, t)$: Glass2-dashed curve) during vitrification. At $T_{0g}$, the system falls off its equilibrium state, whose location depends on the rate of cooling. Structures appear to freeze (over an extremely long period of time) at and below $T_{0G}$; see text. The transition region between $T_{0g}$ and $T_{0G}$ over which the liquid turns into a glass has been exaggerated to highlight the point that the glass transition is not a sharp point. For all temperatures $T_0 < T_{0g}$, any non-equilibrium state along the dotted and dashed curves undergoes structural relaxation in time towards the supercooled liquid. The two vertical downward arrows show isothermal (constant medium temperature $T_0$) structural relaxation at two different temperatures in Glass1, during which the entropy $S(T_0, t)$ decreases in time, as shown by the downward arrows. For Glass2, the entropy $\hat{S}(T_0, t)$ must increase during isothermal structural relaxation. During the relaxation, the temperature $T(t)$ of the system also decreases towards the temperature of the medium in both glasses. The entropy of the supercooled liquid is shown to extrapolate to zero per our assumption, but that of Glass1 to a non-zero value and of Glass2 to zero at absolute zero. The possibility of an ideal glass transition, which does not affect our conclusion, will result in a singular form of the solid curve.
thermodynamics \[1, 2, 3, 7\]. This then explains the symbol over the arrow in Eq. (2) and the header of this subsection. The behavior appears to be the right behavior for the entropy in an isobaric process as the entropy must be an increasing function of the enthalpy with the slope given by

$$\left( \frac{\partial S(t)}{\partial H(t)} \right)_P \approx \frac{1}{T(t)} \geq 0,$$

see Eq. (23); it is well known that the enthalpy falls (rises) during isobaric cooling (heating) \[8\]. The analysis in our previous work \[1, 2\] is carried out for any non-equilibrium system. It is therefore also applicable to glasses where one must, in addition, make a distinction between fast and slow processes. We have considered the issue of the fictive temperature in glasses in our work \[1\], where such a distinction has been made.

**B. Unconventional Approach (UCA) to Glass Transitions**

In a series of papers \[9–11\], Gupta, Mauro and coworkers, to be collectively denoted in short by GMc here, have developed a description of glasses without using any internal variables or any fictive temperature. Even the fictive temperature or pressure, which some people treat as an internal variable, is not considered in their theoretical development, notwithstanding the fact that they are used when GMc consider experimental data. Their conclusion is that their statistical entropy \(\hat{S}(T_0, t)\) for the glass *increases* during relaxation towards \(S_{eq}\)

$$\hat{S}(T_0, t) \xrightarrow{UCA} S_{eq}(T_0);$$

see Glass2 and the portion of the upward thick arrow in Fig. 2 above the horizontal dash; the latter is located at the value of the Glass2 entropy. In the following, we will use \(\hat{S}\) for the statistical entropy used by GMc to distinguish it from the thermodynamic or the Gibbs statistical entropy \(S\) used in our approach. During the glass transition, the entropy \(\hat{S}(t)\) *falls* below \(S_{eq}\) of the supercooled liquid in this approach. Thus, they suggest that the glass transition and relaxation are inverse processes. They also take their glass as homogeneous, just as we have done in our earlier work \[1\]; the difference is that their glass is identified by its temperature \(T_0\), pressure \(P_0\) and its history. Thus, they make no distinction between the instantaneous temperature of the glass and the external temperature of the medium. As the above-mentioned "affinities" vanish, \(\hat{S}(t)\) and \(V(t)\), etc. do not play the role of internal variables. Internal variables are normally used in traditional non-equilibrium
thermodynamics [1, 2, 5–7], although they are very hard to identify, and even harder (really impossible) to control. For the application of internal variables to glasses, we refer the reader to Nemilov [8]. In the absence of any internal variable, the approximation in Eq. (3) turns into an identity [1]; see also Eq. (28). As the behavior of the entropy during relaxation does not obey Eq. (28), we will call their approach the unconventional approach (UCA) in this work; this explains the symbol over the arrow in Eq. (4) and the header of this subsection.

One can understand the drop \( \Delta_{GT} \hat{S}(t) \) in the entropy of Glass2 during a glass transition, provided the entropy of the medium goes up by \( \Delta_{GT} \tilde{S}(t) \) to compensate the loss and some more so that the entropy of \( \Sigma_0 \) does not decrease

\[
\Delta_{GT} S_0(T_0, t) = \Delta_{GT} \hat{S}(T_0, t) + \Delta_{GT} \tilde{S}(T_0, t) \geq 0
\]  

(5)
during the glass transition. However, the authors have not discussed this issue at all. This is not surprising as they neither include any medium in their discussion nor do they consider an isolated system for which Eq. (11) holds. We will always consider \( \Sigma \) as a part of the isolated system \( \Sigma_0 \) and apply Eq. (11) to the latter. This will then allow us to evaluate \( \Delta_{GT} \tilde{S}(t) \). It is the magnitude of \( \Delta_{GT} \tilde{S}(t) \) that would determine whether the entropy of the glass remains above or below \( S_{eq} \) of the supercooled liquid. As the entropy change of the medium is completely reversible, its evaluation will not suffer from any irreversibility going on in \( \Sigma_0 \). This is the major benefit of investigating a glass as part of \( \Sigma_0 \).

Both glasses begin to deviate from the equilibrium supercooled liquid at \( T_{0g} \), but their structures are not yet “frozen;” they freeze over a long period of time (\( t \gg \tau_{obs} \)) at a lower temperature \( T_{0g} \) to form an amorphous solid, to be identified as a glass (Glass1 and Glass2). The location of \( T_{0g} \) is determined by the choice of \( \tau_{obs} \); indeed, \( T_{0g} \) decreases with increasing \( \tau_{obs} \). Over the transition region between these two temperatures, the internal variables gradually change form their equilibrium values at \( T_{0g} \) to their frozen values at \( T_{0G} \).

In the absence of any internal variable, fixing the temperature and pressure fixes the instantaneous state. As the UCA glass (Glass2) is homogeneous and has the same constant temperature and pressure as the medium, it appears then that there cannot be any heat transfer between \( \Sigma \) and \( \tilde{\Sigma} \). If true, then during an isothermal relaxation (constant \( T_0 \) of the medium under isobaric condition), the first law with \( dQ(T_0, t) \) \( \overset{UCA}{=} \) 0 and no internal variables yields

\[
dE(T_0, t) \overset{UCA}{=} -P_0dV(T_0, t) \leq 0;
\]
This implies that \( dV(T_0, t) \geq 0 \) during relaxation, which is most certainly not a rule in glasses.

Another important aspect of glass transition, as has become apparent from recent work, is the violation of the principle of detailed balance and of the fluctuation dissipation theorem \(^{[12]}\), such as the equivalence of the heat capacity with enthalpy fluctuations. But the theorem is shown to be valid in UCA \(^{[11]}\), which is quite surprising.

Faced with these hard to understand consequences and the conflict with our own results, we decided to examine the basic assumptions in the unconventional approach. These assumptions, to the best of our reading of their work, are not properly and adequately justified so far by GMc. In many cases, they are simply stated as facts alongside several statements that are either exaggerations or are outright false. Therefore, we will treat them as conjectures and investigate whether we can justify them either rigorously or on physical grounds. We defer to the next section these conjectures and the role they play in the logical development of UCA.

We should mention at this point that some aspects of UCA have already been criticized by other authors \(^{[13–19]}\). In particular, Goldstein \(^{[13]}\), see also \(^{[17, 18]}\), demonstrated that the entropy loss during the glass transition violates the second law. To this GMc responded by suggesting that the process of glass formation is not governed by the second law \(^{[20]}\). This is a surprising response (as the second law is supposed to govern all processes), but quite understandable as GMc have a very unconventional view of the second law. We do not get into this debate by avoiding the issue altogether. We focus on an isolated system \( \Sigma_0 \), where there cannot be any dispute about the second law; see Eq. \(^{(1)}\). In that sense, our work differs from other attempts \(^{[13, 14, 19]}\). In our investigation, which is at a fundamental level, we look at all the underlying assumptions of UCA to see if they can be justified so that UCA could become an acceptable theory. We only consider the thermodynamic entropy during this part of our investigation, so we do not get confused by which statistical entropy formulation is appropriate to study vitrification. Once, we settle the issues by using the thermodynamic entropy, we turn to the statistical formulation of entropy to assess the notion of statistical entropy GMc have advocated. It is our belief that the unconventional view of the second law and of the statistical entropy form the basis of UCA, which has been justified in various publications by following the logical steps listed below:
UCA1. The use of equilibrium thermodynamics using calorimetric data cannot determine the entropy of the glass.

UCA2. Thus, there is no reason for the residual entropy to exist at absolute zero.

UCA3. The entropy of a single microstate is zero. As a glass is in one microstate at absolute zero, its entropy must be zero in accordance with the third law.

UCA4. The glass undergoes spontaneous relaxation during which the entropy increases and reaches that of the equilibrated supercooled liquid given by the solid curve in Fig. 2 from below.

UCA5. The entropy drop due to the loss of ergodicity and the spontaneous relaxation with entropy increase are, therefore, inverse processes.

UCA6. A calculation method for the entropy is developed to show drop in the entropy during the glass transition region, see Glass2 in Fig. 2 so that the calculated entropy shows no residual entropy at absolute zero.

It is important to understand their final conclusion, the so-called inverse relationship (UCA5) and to see if it, and all of its underlying assumptions (UCA1-UCA4), are consistent with the second law, the only fundamental law of Nature that is accepted by all including GMc. Various conjectures leading to UCA5 seem not to be adequately answered so far by GMc. This deficiency by itself does not mean that UCA is unfounded, but it does mean that it requires closer scrutiny, which forms the basis of this investigation. These authors invariably consider their system $\Sigma$ (the glass) at fixed $T_0$ and $P_0$, which means that it is not an isolated system; rather, it is surrounded by $\tilde{\Sigma}$; see Fig. 1. (In the following, we will call their system $\Sigma$ an open system, knowing very well that this is not the customary usage. We believe that this will not cause any confusion.) As GMc constantly appeal to the second law in terms of the entropy of the system, the most convenient way to examine their approach is to focus on the isolated system $\Sigma_0$ in which the glass will be a possible state of the system $\Sigma$. This allows us to examine their approach at the most fundamental level.
C. Summary of Results

We summarize our conclusions that follow from the application of the second law in terms of entropy to an isolated system. We only consider vitrification in the rest of the work. We agree with UCA1, but we find UCA2 unsubstantiated. Indeed, we find the calorimetrically obtained $S_{\text{expt}}(T_0)$ forms a lower bound to the entropy $S(T_0)$ so that the residual entropy has a lower bound $S_{\text{expt}}(T_0)$ at absolute zero. The latter entropy is usually non-negative, so that the residual entropy must be even larger than this. Such a glass cannot satisfy the third law, which leads to UCA3 being invalid. Indeed, if there is ever any conflict between the second and the third law, it is the former that supersedes. In an isothermal relaxation, the entropy actually decreases towards the equilibrated supercooled liquid entropy, thus invalidating UCA4. However, the irreversible entropy generation remains non-negative in accordance with the second law. GMc do not recognize the importance of the irreversible entropy generation for the second law and mistakenly ascribe its universal non-negative aspect to the entropy of the system. Following UCA, we find that $\hat{S}(t) = 0$ all times including $t = 0$, when the external condition (such as the temperature) of the system is changed. This is inconsistent with UCA5. Even if we follow UCA Conjecture 3 see Sect. 11, although it is inconsistent with the first part, we find that the entropy now increases at $t = 0$ and reaches that of Glass2 at $t = t_{\text{obs}}$; the glass transition occurs at this instant if the external condition of the system is disturbed somehow. If it is not disturbed, the entropy would continue to increase. Thus the entropy is always increasing for $t \geq 0$ in UCA. In both cases, we do not find that there is any justification in calling the glass transition and relaxation to be inverse processes in UCA. Thus, UCA5 is not a consequence of the previous steps UCA1-UCA4. Just because GMc have provided a computational scheme to support their invalid conclusion cannot be considered a proof of the validity of UCA. We find that UCA misses out many important aspects of non-equilibrium systems such as their temperature, pressure, etc. being different from those of the medium, absence of any internal variables to capture additional irreversible entropy generation, the failure of the fluctuation-dissipation theorem etc.
II. IMPORTANT CONJECTURES IN UCA

As the recent work from GMc is expected to represent their most up-to-date and current state of understanding of various issues, we will mostly focus on their recent work [11] for an understanding of the technical aspect of their approach, the cornerstone of which is that it treats structural relaxations as the inverse of the glass transition [11]:

**Conjecture 1** The inverse of the glass transition is structural relaxation, which involves a restoration of ergodicity as a glass spontaneously approaches the liquid state. This spontaneous relaxation process is called a unifying process and must entail an increase in entropy as the observation time constraint is lifted.

The decrease in entropy during glass transition to that of Glass2 is justified on the basis of a seemingly innocuous conjecture about the effect of confinement to an ergodic component stated as a fact [11]:

**Conjecture 2** The loss of ergodicity at the glass transition necessarily involves a loss of configurational entropy, since this causes the system to be confined to a subset of the overall phase space. At absolute zero, any glass is confined to one and only one microstate, so the configurational entropy of a glass is necessarily zero, in accordance with the Third Law and the principle of causality.

In vitrification, the entropy does decrease. This is most clearly seen by quenching the supercooled liquid from a temperature just above $T_{0g}$ to A below $T_{0g}$; see Fig. 2. The decrease is shown by the dashed downward arrow to B, which represents the entropy of Glass1 that stays above $S_{eq}$. A similar drop of much higher value occurs for Glass2. Both glasses seem to conform to the first part of the conjecture. Therefore, this part cannot be the defining characteristics of ergodicity loss or UCA. It is merely a consequence of a positive heat capacity and nothing more and has nothing to do with ergodicity loss. Whether the loss is big enough to satisfy Eq. (4) is never demonstrated as they have not calculated the entropy gain $\Delta GT S(T_0, t)$ of the medium. The second half of the conjecture requires the entropy to vanish at absolute zero, so the entropy of the UCA glass is given by the dashed curve Glass2 in Fig. 2 and not by the dotted curve Glass1. Thus, UCA requires the entropy to drop below $S_{eq}$ of the equilibrated supercooled liquid and requires evaluating $\Delta GT S(T_0, t)$ to substantiate it. This part of the conjecture is based on the following conjecture [9]:
**Conjecture 3** . . . an instantaneous measurement . . . causes the system to “collapse” into a single microstate $i$ with probability $p_i(t)$. In the limit of zero observation time, the system is confined to one and only one microstate and the observed entropy is necessarily zero. However, the entropy becomes positive for any finite observation time $\tau_{\text{obs}}$ since transitions between microstates are not strictly forbidden except at absolute zero, barring quantum tunneling.

The conjecture refers to a system ”collapsing” into one out of many microstates and asserts as a fact that the entropy of a microstate is identically zero without any supporting justification. This creates some conceptual problems. At each instant of time $t$, any system, not necessarily a glass only, is going to be in some microstate $i_t$; of course, we do not know which microstate it would be in at that instance. If we make ”an instantaneous measurement,” the system will remain in that microstate; there is no ”collapse” of the microstate. Even the macrostate, which is by definition the collection of all relevant microstates along with their probabilities, does not have time to change, because the probability distribution $p_i(t)$ does not change. Indeed, one does not need to make any measurement on the system to conclude ”...the system to collapse into a single microstate...” At each instance, the system is going to be in some microstate. If we interpret a measurement as something that instantaneously alters the external condition such as the fields of the medium, then such an instantaneous move (measurement) will probe the instantaneous microstate of the system. The statistical entropy of the system $\hat{S}(t) = 0$ at each instant, and therefore at all times, in accordance with Conjecture 3. This is true even if the system is an isolated system not in equilibrium. This concept of statistical entropy in UCA is in direct contradiction with the second law in Eq. (1) according to which the thermodynamic entropy $S_0(t)$ is not constant in time. Thus, the conjecture needs some justification, which GMc have not provided so far. In particular, it allows us to make the following

**Remark 4** The statistical concept of entropy used by GMc in the above conjecture has nothing to do with the thermodynamic entropy used in Eq. (1).

Another conceptual problem is that the statistical entropy is defined for a macrostate as an average quantity over all microstates; see Eq. (29). If it happens that a certain macrostate consists of a single microstate whose probability must be $p(t) = 1$, then the
statistical entropy of that macrostate such as a completely ordered crystal is certainly zero. But what does one mean by the statistical entropy, an average quantity, of a microstate? What averaging does one perform for a microstate? This issue is never addressed by GMc except by the above conjecture and by an appeal to the Boltzmann entropy formulation 
\[
\hat{S}(t) = \ln W(t) \quad (\text{we set } k_B = 1),
\]
which requires the number of microstates \(W(t)\) forming the macrostate. This is evident from [11].

**Conjecture 5** . . . *Boltzmann’s definition of entropy is the only one valid and consistent with the Second Law for non-equilibrium system.*

They take \(W(t) = 1\) for a single microstate at all temperatures, even if there may be other possible microstates, and argue for zero entropy. Thus, the instantaneous statistical entropy will always be zero at all times and at all temperatures since the system is in a single microstate at each instant. The idea of introducing an instantaneous measurement is highly appropriate as we need to measure instantaneous values of the observables. No measuring apparatus will ever measure the instantaneous entropy; its value can only be inferred indirectly. Thus, entropy is not an observable in the same sense as the mechanical variables such as energy, volume, etc. are; it is a thermodynamic quantity, which has been given a statistical interpretation in statistical mechanics. Despite this, GMc argue that, when the measurement takes some non-zero time, the statistical entropy increases with the duration of measurement. However, GMc never clarify if the measurement gives an accumulated value or the average value of any quantity. The first option is counter-intuitive as this suggests that the value of the energy by such a measurement will increase with the duration of the measurement. The second option seems reasonable as the value of the measurement will give an average energy. This then suggests that, since at each instant during the measurement, the system is in a single microstate so that its entropy is zero, the measurement will still result in a zero entropy. Why does it increase? Even if we adopt the first option, then the ”measured” entropy would still be zero as accumulating zero always gives zero. No explanation is offered by GMc for this part of the conjecture. Recall that one cannot appeal to the second law, which uses the thermodynamic entropy, while GMc use their statistical entropy whose equivalence with the thermodynamic entropy is never shown by them. We have addressed this issue elsewhere [15, 16, 21, 22] with a very different conclusion. We find, see Sect. [V], that the statistical entropy contribution of a microstate \(i\) is
− ln \( p_i(t) \), which is inconsistent with the above conjecture. Thus, we need to understand the basis of their conjecture. This conjecture is amplified by the following two inter-connected Conjectures [10]:

**Conjecture 6** With Boltzmann’s definition, the entropy increases during a spontaneous process.

**Conjecture 7** If entropy increases during the relaxation process and the glass transition is the inverse of relaxation, then entropy must decrease during the glass transition. This is consistent with our previous conclusion that the glass transition is nonspontaneous. While this conclusion may appear as inconsistent with the second law, there is no violation since the second law is a statement about spontaneous processes, i.e., processes in which a system relaxes toward an equilibrium or less constrained state. The glass transition is not such a process since here an equilibrium system becomes a constrained equilibrium state.

Conjecture 6 is not only inconsistent with Conjecture 3, it is inconsistent with classical thermodynamics when we consider a system which is not isolated. For such a system, its relevant free energy decreases in any spontaneous process. It appears that GMc confuse isothermal relaxation occurring in a glass with spontaneous processes occurring at fixed observables such as energy, volume, etc. The latter processes occur for isolated systems, not for a glass at fixed temperature and pressure. If GMc insist on focusing on the entropy, then the statement should be in terms of the irreversible entropy generation \( \Delta_i S(t) \geq 0 \), not in terms of the entropy change \( \Delta S(t) \). Thus, for the conjecture to make sense, the reversible entropy drop \( \Delta_e S(t) \) during vitrification must not be too negative to ensure \( \Delta S(t) > 0 \). This requires a justification that

\[
|\Delta_e S(t)| < \Delta_i S(t)
\]

for the conjecture to be valid. However, no such justification is offered by GMc in their work. As given, it gives the impression that UCA treats entropy to increase during relaxation in all kinds of systems, isolated or not. This is unsettling. The same problem occurs with the last conjecture.

Therefore, to determine whether the above conjectures are justifiable, we turn to the second law for \( \Sigma_0 \).
III. CONSEQUENCES OF THE SECOND LAW FOR $\Sigma_0$

A. Irreversible Entropy Generation

The second law does tell us that the irreversible entropy generation in any spontaneous process is non-negative, but leaves the behavior of the entropy undetermined; the latter depends on the process. The entropy that appears in the second law in classical thermodynamics is a thermodynamic concept. It is postulated to exist even when the system is not in equilibrium; its existence and continuity neither requires any statistical interpretation nor does it require the third law. If there is any conflict between the second law and any other laws of physics, the second law will always win. In general, in any thermodynamic process from macrostate 1 to macrostate 2, the change in the entropy

$$\Delta S \equiv S_2 - S_1 = \Delta_e S + \Delta_i S, \quad \Delta_i S \geq 0,$$

(6)

in which $\Delta_i S$ denotes the irreversible entropy generation within the system and $\Delta_e S$ denotes the reversible entropy change due to exchange with the medium. The actual value of $\Delta S$ will depend on the values of $\Delta_e S$ and $\Delta_i S$, and can have any sign. In general, we have

$$\Delta S \geq \Delta_e S,$$

(7)

which will prove extremely important below. In the following, we will only be interested in vitrification for which $\Delta_e S$ is negative. If it happens that $\Delta_e S$ is negative enough to overcome the positive contribution of $\Delta_i S$, then we will obtain a negative $\Delta S$.

B. Second Law for $\Sigma_0$

For an isolated system such as $\Sigma_0$, $\Delta_e S = 0$ so it is not surprising that

$$\Delta S^\text{isolated system} \equiv \Delta_i S \geq 0,$$

(8)

which explains the standard formulation of the second law but only for an isolated system. We now consider $\Sigma_0$, but we allow the system to be not in equilibrium with the medium. The medium is at a fixed temperature $T_0$ and pressure $P_0$. We are thinking of the system that has been brought in contact with the medium at some instant $t = 0$, which we then
follow in time. The entropy of $\Sigma_0$ is written as a sum of the entropies of the system $S(t)$ and the medium $\tilde{S}(t)$:

$$ S_0(t) = S(t) + \tilde{S}(t). \quad (9) $$

During its approach towards the maximum, the instantaneous temperature, pressure, etc. of the system, if they can be defined, are different from those of the medium $[1, 2, 4]$. The condition required for defining temperature, pressure, etc. of any non-equilibrium system is that its entropy is a function of its instantaneous observables and internal variables $[1, 2, 5–7]$ only; it has no explicit time-dependence. The system is said to be in internal equilibrium $[1, 2]$, when this condition is met. Unless this condition is met, we cannot identify fields for the system, even though they exist for the medium. For simplicity, we will consider a system with a fixed number of particles with only observables $E(t)$ and $V(t)$ along with just one internal variable $\xi(t)$. Thus,

$$ S(t) \equiv S(E(t), V(t), \xi(t)). \quad (10) $$

At each instance, $E(t), V(t)$ and $\xi(t)$ depend on the history of the system. The corresponding fields are now given by respective derivatives of the entropy:

$$ \frac{1}{T(t)} = \left( \frac{\partial S(t)}{\partial E(t)} \right), \quad \frac{P(t)}{T(t)} = \left( \frac{\partial S(t)}{\partial V(t)} \right), \quad \frac{A(t)}{T(t)} \equiv \left( \frac{\partial S(t)}{\partial \xi(t)} \right); $$

the new variable $A(t)$ represents the affinity conjugate to $\xi(t)$. The Gibbs fundamental relation is given by

$$ dS(t) = \frac{1}{T(t)} dE(t) + \frac{P(t)}{T(t)} dV + \frac{A(t)}{T(t)} d\xi(t), \quad (11) $$

which can be rewritten as

$$ dE(t) = T(t) dS(t) - P(t) dV(t) - A(t) d\xi(t) \quad (12) $$

for the non-equilibrium system. In equilibrium, this relation will reduce to

$$ dE = T_0 dS - P_0 dV, \quad (13) $$

where all variables are independent of time and we have used the fact that the equilibrium value $A_0$ of $A(t)$ vanishes. We can rewrite Eqs. (11) and (12) in the following form $[2]$

$$ dS(t) = \frac{1}{T_0} dE(t) + \frac{P_0}{T_0} dV + \left[ \frac{1}{T(t)} - \frac{1}{T_0} \right] dE(t) + \left[ \frac{P(t)}{T(t)} - \frac{P_0}{T_0} \right] dV + \frac{A(t)}{T(t)} d\xi(t), \quad (14) $$

$$ dE(t) = T_0 dS(t) - P_0 dV(t) + [T(t) - T_0] dS(t) - [P(t) - P_0] dV(t) - A(t) d\xi(t). \quad (15) $$
The last three terms in Eq. (14) each give three distinct irreversible entropy generation terms, and must be individually non-negative in accordance with the second law. Let us consider the middle term in this equation, which is non-negative. In a vitrification process, the energy of the system decreases so that \( dE(t) \) is negative. Thus, in a vitrification process, \( T(t) > T_0 \) during isothermal relaxation (constant \( T_0 \)) and approaches \( T_0 \) from above as the relaxation ceases after equilibrium is achieved\[1\]. As this is a general result coming from the second law, it must be valid for all non-equilibrium systems including glasses. We need to see whether both glasses shown in Fig. 2 satisfy this result.

For the enthalpy \( H(t) \equiv E(t) + P_0 V(t) \), we find

\[
dH(t) = T_0 dS(t) + V(t) dP_0 + [T(t) - T_0]dS(t) - [P(t) - P_0]dV(t) - A(t)d\xi(t).
\]

(17)

Let us consider the consequences of the second law. From now on, we focus on isobaric processes carried out at a fixed pressure \( P_0 \) of the medium. We will assume that in such an isobaric process, \( P(t) = P_0 \) at all times. For the time derivative of the entropy \( S_0 \) of the isolated system at fixed \( T_0 \), it can be shown \[1, 2\] that in terms of the enthalpy and the internal variable of the system

\[
\frac{dS_0(t)}{dt} = \left( \frac{1}{T(t)} - \frac{1}{T_0} \right) \frac{dH(t)}{dt} + \frac{A(t)}{T(t)} \frac{d\xi(t)}{dt} \geq 0.
\]

(18)

Each term on the right side of the first equation gives an irreversible entropy generation, see Eq. (8), and must be non-negative. Accordingly,

\[
\left( \frac{1}{T(t)} - \frac{1}{T_0} \right) \frac{dH(t)}{dt} \geq 0.
\]

(19)

which is unaffected by the number of internal variables. With Eq. (16), this shows that

\[
dH(t)/dt \leq 0,
\]

(20)

which is found to hold in vitrification.

C. Determination of \( \Delta_{GT} S(T_0, t_{obs}) \) and \( \Delta_{GT} \tilde{S}(T_0, t_{obs}) \)

From Eqs. (14) and (18), we find that

\[
\frac{dS(t)}{dt} = \frac{1}{T(t)} \frac{dH(t)}{dt} + \frac{A(t)}{T(t)} \frac{d\xi(t)}{dt}, \quad \frac{d\tilde{S}(t)}{dt} = -\frac{1}{T_0} \frac{dH(t)}{dt};
\]

(21)
the two equations give the rate at which the entropy of the system and of the medium change. In vitrification, the rate for the medium is positive. The second term in the entropy rate for the system is non-negative.

The rate of the entropy drop is given by

\[ \left| \frac{dS(t)}{dt} \right| = \frac{1}{T(t)} \left| \frac{dH(t)}{dt} \right| - \frac{A(t)}{T(t)} \frac{d\xi(t)}{dt} \leq \frac{1}{T(t)} \left| \frac{dH(t)}{dt} \right| \leq \frac{d\tilde{S}(t)}{dt}, \]

so that the rate of entropy drop for the system is bounded from above by the rate of entropy gain of the medium. Thus, the drop \( |\Delta S| \) for \( \Sigma \) is bounded from above by the entropy gain \( \Delta \tilde{S} \) during some interval \( \Delta t \):

\[ |\Delta S| \leq \Delta \tilde{S}, \]

where we have introduced the change in any thermodynamic quantity \( F \):

\[ \Delta F(t) \equiv F(t) - F(t = 0). \]

From Eq. (21), we find that

\[ \Delta_v S(t) = \frac{1}{T_0} \Delta H(t), \quad \Delta_i S(t) = \int_0^t \frac{\dot{H}(t)}{T(t)} dt - \frac{\Delta H(t)}{T_0} + \int_0^t \frac{A(t) \dot{\xi}(t) dt}{T(t)}, \quad \Delta_u \tilde{S}(t) = -\frac{1}{T_0} \Delta H(t), \]

where the dot above a symbol represents the time-derivative. The maximum entropy drop \( |\Delta S| \) occurs when \( \Sigma \) comes to equilibrium with the medium. In this case, \( T(t) \to T_0 \) and \( A(t) \to 0 \). It is also equal to the maximum entropy gain of the medium at equilibrium. This situation correspond to the system as the equilibrated supercooled liquid with its entropy \( S_{eq} \) given by the solid curve in Fig. 2. Thus, we conclude that the entropy of the non-equilibrium system always stays above that of the supercooled liquid

\[ S(T_0, t) \geq S_{eq}(T_0) \]

during vitrification. During relaxation, \( S(T_0, t) \) approaches \( S_{eq}(T_0) \) from above so that

\[ \frac{dS(t)}{dt} \leq 0; \quad (22) \]

this conclusion is valid regardless of the number of internal variables. The equality occurs only when equilibrium with the medium has been achieved.

We can understand this result on physical grounds as follows. Let \( T'_0 > T_{0g} \) denote the temperature from which the system is cooled by bringing the system in contact with the
medium at $T_0 < T_{0\text{g}}$ at $t = 0$; see point A in Fig. 2. This situation corresponds to a rapid quench. Right after the contact, the system has not had any time to change its microstate and remains in the microstate it had just prior to the contact is established. Thus, at $t = 0$, the system has the older entropy $S_{\text{eq}}(T_0')$ of the equilibrated supercooled liquid at the previous temperature. We will justify this fact later; see Eq. (33). The equilibrium entropy $S_{\text{eq}}(T_0)$ must be lower than $S_{\text{eq}}(T_0')$ since $T_0 < T_0'$. Therefore, the entropy must continue to drop during relaxation at $T_0$ even if the contribution from $\dot{\xi}(t)$ is non-negative. This gives us the entropy of Glass1 at $t = t_{\text{exp}}$. The derivation of the last equation given in [1] was simpler as we had not considered the internal variable $\xi(t)$ there. The above discussion justifies the behavior in the conventional approach described by Eq. (2).

From Eqs. (20), (21) and (22), we find

$$\frac{dS(t)}{dH(t)} = \frac{1}{T(t)} \left[ 1 + A(t) \frac{d\xi(t)}{dH(t)} \right] \geq 0,$$

which proves Eq. (3). This equation differs from the one given in [1], see Eq. (28) because of the contribution from the internal variable, which was not considered there. However, the sign of the ratio remains the same.

From Eq. (21), we find

$$\Delta \tilde{S}(t) \equiv \tilde{S}(t) - \tilde{S}(t = 0) = -\frac{\Delta H(t)}{T_0} = -\frac{H(t) - H(t = 0)}{T_0}$$

At the glass transition, we then have

$$\Delta_{\text{GT}} \tilde{S}(T_0, t_{\text{obs}}) \equiv -\frac{H(T_0, t_{\text{obs}}) - H(T_0, t = 0)}{T_0} \leq \frac{H(T_0, t = 0) - H_{\text{eq}}(T_0)}{T_0} \equiv \Delta_{\text{eq}} \tilde{S}(T_0),$$

where $\Delta_{\text{eq}} \tilde{S}(T_0)$ is the maximum entropy gain of the medium, which occurs when the system has come to equilibrium with the medium. This gain can be easily obtained by using a reversible path from the initial temperature $T_0'$ to the final temperature $T_0$. This means that in Fig. 2 the system continues along the equilibrated supercooled liquid. Thus,

$$\Delta_{\text{eq}} \tilde{S}(T_0) = -\Delta_{\text{eq}} S(T_0) \equiv S_{\text{eq}}(T_0') - S_{\text{eq}}(T_0).$$

In such a reversible process, $\Delta S_0 = 0$, as expected.

Let us compare this entropy drop with that in the system. Because of the non-negative contribution from $\dot{\xi}(t)$, the entropy change $\Delta_{\text{GT}} S(T_0, t)$ satisfies

$$|\Delta_{\text{GT}} S(T_0, t_{\text{obs}})| \leq \int_0^{t_{\text{obs}}} \frac{H(t)}{T(t)} dt \leq \frac{\Delta_{\text{GT}} H(t_{\text{obs}})}{T_0} \equiv \Delta_{\text{GT}} \tilde{S}(T_0, t_{\text{obs}}) \leq \Delta_{\text{eq}} \tilde{S}(T_0).$$

(24)
Thus, the entropy change of the medium and of the system satisfy Eq. (5) at the glass transition. But most importantly, the entropy loss of the medium cannot exceed $|\Delta_{eq}S(T_0)|$, so that

$$|\Delta GTS(T_0, t_{obs})| \leq \Delta_{eq}\tilde{S}(T_0) = |\Delta_{eq}S(T_0)|.$$  \hspace{1cm} (25)

We thus conclude \[1, 2\] that the entropy of the glass must stay above that of the equilibrated supercooled liquid, which makes Glass1 as the physical glass, a conclusion based on the second law.

We can now extend the discussion to continuous cooling as follows. We take $T'_0 > T_{0g}$ and $T_0^{(1)} = T_{0g} - \Delta T_0$, and wait for $\Delta t = t_{obs}$. The entropy is that of Glass1 at $T_0^{(1)}$. We now decrease the temperature by $\Delta T_0$ to $T_0^{(2)} = T_{0g} - 2\Delta T_0$, and wait for $\Delta t = t_{obs}$. The entropy is that of Glass1 at $T_0^{(2)}$. We follow this cooling until the entire Glass1 curve is obtained. At each temperature, the entropy of the glass must stay above $S_{eq}$ of the equilibrated supercooled liquid. We have thus proved the following important theorem for any non-equilibrium system:

**Theorem 8** The entropy of any non-equilibrium system such as a glass in isobaric cooling must stay above that of the equilibrated state.

**D. Thermodynamic Entropy and Glasses**

In the above discussion, which starts with the second law behavior of the thermodynamic entropy $S_0(t)$ of $\Sigma_0$, no assumption about the form of the thermodynamic entropy $S(t)$ (such as whether $S(t)$ lies above (Glass1) or below (Glass2) the entropy of the equilibrated supercooled liquid; see Fig. 2) or the nature of irreversibility such as loss of ergodicity, chemical reaction, chaos, phase transition, etc. in the system is made. We do not impose any statistical interpretation on these entropies either; they are assumed to exist as thermodynamic quantities in classical thermodynamics. Thus, their values are not relevant; all that is relevant is their rate. Accordingly, we do not have to even worry if the entropies needed to be treated as statistical quantities with certain particular formulation of entropy (Boltzmann versus Gibbs, or the modification in UCA). Any attempt to identify these classical entropies statistically must still conform to the consequence of the second law expressed, for example, in Eq. (22) during vitrification.
Although no assumption was made regarding $S(T_0, t)$ lying above or below the entropy $S_{eq}(T_0)$ of the equilibrated supercooled liquid, the second law has resulted in Glass1 as being the physically relevant glass, and not Glass2. The deviation of Glass1 entropy $S(T_0, t)$ from $S_{eq}(T_0)$ of the solid curve is due to the irreversible contributions. The entropy of the non-equilibrium state Glass1 approaches that of the equilibrated supercooled liquid entropy from above during isothermal relaxation. This downward approach of the entropy of Glass1 is a consequence of the second law. The entropy of the system, however, defined, must satisfy Eq. (22) in vitrification if the system has to obey the second law.

We assume that at time $t = 0$, the system is above $T_{0g}$, so that the system is an equilibrated supercooled liquid. Its temperature and pressure are equal to those of the medium. Let the $E', V'$ and $S'$ denote the energy, volume, and entropy of the equilibrated supercooled liquid at this temperature $T'_0$, respectively. The equilibrium value of the internal variable is denoted by $\xi'$. At time $t = 0$, we abruptly bring this system in contact with another medium at temperature $T_0$ just below $T_{0g}$; see for example point A in Fig. 2. Immediately after the contact, the initial state of the system is characterized by its observables $E', V', \xi'$ and $S'$ at $T_0$. After some time $t = t_{exp}$, the system appears to be glassy as shown by B on Glass1. During further relaxation, the system eventually approaches the equilibrated supercooled liquid at $T_0$. During the relaxation process, the entropy $S(T_0, t)$ decreases in accordance with Eq. (22). This is an example of a fast quench. In a continuous vitrification process carried out at a fixed rate, the resulting glass entropy is shown by Glass1. If such a glass is allowed to relax, see the two downward arrows, it also converges to the solid curve of the supercooled liquid. The resulting entropy during heating is shown by the dash-dotted curve (a) and shows the resulting hysteresis over the transition region.

With the above background about the role of the second law for the open system, we turn to UCA to see if we can justify its consequences or assumptions/conjectures.

**IV. IRREVERSIBLE CONTRIBUTIONS AND CALORIMETRIC CALCULATION DURING THE GLASS TRANSITION**

GMc assert in the abstract: A common assumption in the glass community is that the entropy of a glass can be calculated by integration of measured heat capacity curve through the glass transition. Such integration assumes that glass is an equilibrium material and that
the glass transition is a reversible process...” This is an inaccurate and highly misleading statement, which completely overlooks the tremendous progress made by Prigogine and Defay [23], Davies and Jones [24] and others who have followed the concept of internal variables due to de Donder [1, 2, 5–7]. We refer the reader to a very nice review by Nemilov [14] and his monogram [8]. Workers in the glass community are well aware of the fact, see Fig. 2, that the glass transition neither occurs at a single temperature (it actually occurs over a range $T_{0G} - T_{0g}$) nor is it reversible (see the dotted curve and the dash-dotted curve (a) for the entropy during cooling and heating for Glass 1). Any attempt to use equation 1 of GMc [11], which we slightly modify to express it in terms of the thermodynamics entropy and present below

$$\Delta S \equiv S(T_0) - S(T_M) = \Delta e S \equiv \int_{T_m}^{T_0} \frac{C_P(T'_0)}{T'_0} dT'_0,$$  

by workers in the field merely reflects the desire to use an approximate description by replacing $S(T_0)$ by its calorimetric value $S_{\text{expt}}(T_0)$

$$S_{\text{expt}}(T_0) \equiv S(T_M) + \int_{T_m}^{T_0} \frac{C_P(T'_0)}{T'_0} dT'_0$$

the right hand side in the above equation [11]. Comparing with Eq. (7) shows that the approximation is simply to replace the forward inequality by a forward approximate equality (approximate equality from the greater side)

$$\Delta S \gtrless \Delta e S,$$           (27)

and the question one should ask is: How reliable is the forward approximation [13, 15, 25]? This question has also been recently answered by Johari and Khouri [19]. This forward approximation cannot be confused with the above-mentioned ”common assumption” of equality $\Delta S_{\text{GMc}} \equiv \Delta e S$ in Eq. (26). It appears that GMc confuse this forward approximation with an equality and use it (see below) to suggest that the traditional view of glasses is inapplicable [11]. This suggestion is not the right conclusion.

An important aspect of non-equilibrium systems is that their fields such as the temperature $T(t)$ are different from the constant fields such as the temperature $T_0$ of the surrounding medium. Such a two-field description captures the essence of non-equilibrium states and is also consistent with the violation of the fluctuation dissipation theorem [12] in non-equilibrium systems. It has become apparent that non-equilibrium systems violate
the principle of detailed balance and the fluctuation dissipation theorem. The way irreversibility and the second law are taken into account is by instantaneous fields and the introduction of internal variables; the latter is a standard practice in non-equilibrium thermodynamics, but their role is not considered in UCA. This leads them to make several inaccurate statements. Not realizing that their Eq. (1) is a forward inequality

\[ S(T_0) \geq S_{\text{expt}}(T_0) \]

due to all irreversible contributions to the entropy, see the last three terms in Eq. (14), they incorrectly conclude "... that glass is treated strictly in the framework of equilibrium thermodynamics,..." If the correction is made and the equality is replaced by a forward inequality, it immediately rules out any contradiction with the statement "...that glass is exempt from the Third Law due to its nonequilibrium nature..." since the entropy of the glass at absolute zero is bounded below by \( S_{\text{expt}}(0) \)

\[ S_{\text{res}} \equiv S(0) \geq S_{\text{expt}}(0). \]

One then discovers that there is no contradiction in logic in the traditional view, and the following statement in UCA is without any scientific merit:

"Previous reports of a finite residual entropy of glass at absolute zero are an artifact of treating glass within the context of equilibrium thermodynamics or equilibrium statistical mechanics, assuming ergodicity and without accounting for the observation time constraint."

Not appreciating the important role played by instantaneous fields in non-equilibrium systems leads them to doubt the applicability of

\[ dS \equiv dQ(t)/T(t) \]

due to heat flow to such non-equilibrium systems, where \( dQ \) is the heat transfer with the medium. That it is the correct result follows immediately from Eq. (12) by rewriting it in the form of the first law as

\[ dE(t) = dQ(t) - P(t)dV(t) - A(t)d\xi(t) \]
so that

\[ dQ(t) = T(t) dS(t). \]

The irreversible entropy generation within the system is given by \( d_i S \equiv dQ \{ 1/T(t) - 1/T_0 \} \geq 0 \). In vitrification, \( dQ < 0 \), which then requires \( T(t) \geq T_0 \). This yields \( dS \geq d_e S \equiv dQ/T_0 \), which results in \( S(T_0) \geq S_{\text{expt}}(T_0) \) as noted above. The equality occurs only in equilibrium. However, GMc [11] confuse the forward approximate equation 1 of GMc [11], reproduced here as Eq. (26), with an equality and mistakenly conclude that the classical view is inapplicable. The conclusion is without any foundation. The second law clearly establishes that residual entropy is real. As a non-zero residual entropy is in conflict with the third law can only mean that the third law is not applicable to non-equilibrium systems, a conclusion well known in theoretical physics [30].

As GMc do not consider any internal variable, we must consider Eq. (23) by setting \( A(t) = 0 \). In that case, we have

\[
\left( \frac{\partial S(t)}{\partial H(t)} \right)_p = \frac{1}{T(t)} \equiv \frac{1}{T_0} > 0,
\]

since the temperature of the system is taken equal to \( T_0 \) in UCA. We then conclude that the increase in their statistical entropy along with the decrease in enthalpy during relaxation violates the positivity of the instantaneous temperature of the system and throws doubts that their statistical entropy can be identified with the thermodynamic entropy. As the nature of the statistical entropy is crucial to understand the reasons for the possible failure of \( \hat{S}(t) \), we turn to this issue in the following section.

V. STATISTICAL ENTROPY FOR NON-EQUILIBRIUM SYSTEMS

A. Statistical Entropy as an average for a Macrostate

The discussion so far has been about the thermodynamic entropy and its existence as used in classical thermodynamics and in the formulation of the second law for an isolated system; see Eqs. (8) and (1). All that is required for this is the fact that there exists an entropy function \( S_0(t) \), which is non-decreasing in time. Its actual value is not relevant; all that is relevant is the change in this function. In other words, the thermodynamic entropy is not constrained by the third law in any way; the latter becomes relevant only for the
statistical interpretation of the thermodynamic entropy. The latter does not even have to be non-negative, as is well known from the entropy of an ideal gas at low temperatures. The existence of $S_0(t)$ immediately leads to the existence of $S(t)$ and $\tilde{S}(t)$; see Eq. (9). However, it should be emphasized that whatever value any of these entropies such as $S(t)$ has at any instance, it has this value even if no measurement is made on the system:

**Remark 9** Any statistical interpretation of the entropy must obey the property that its value must be unaffected by the measurement.

This point should not be overlooked. We will explain later how this statement is justified in classical thermodynamics or non-equilibrium statistical dynamics.

We now turn to the statistical interpretation of entropy that provides a justification of the third law for equilibrium states and endow the entropy such as $S_0(t)$ with a definite value. Let $i$ denote a microstate of the isolated system $\Sigma_0$ in some macrostate. The formulation by Gibbs in terms of the probability $p_i(t)$ of a microstate $i$ at time $t$ is as follows:

$$S_0(t) \equiv -\sum_i p_i(t) \ln p_i(t) \equiv -\langle \eta(t) \rangle,$$

where the sum is over all microstates, whose number is $W_0$, associated with the particular macrostate; we have set $k_B = 1$. A microstate is called *available* at time $t$ if its probability is non-zero; otherwise, it is *unavailable* at that time [16]. An available microstate does not mean that the microstate has necessarily been visited by the system during the time interval $t$. Following Gibbs [31], we have introduced the *index of probability*

$$\eta(t) \equiv \ln p(t),$$

so that the entropy becomes a statistical average of the negative index of probability *over* all microstates belonging to the macrostate. This makes entropy similar to any other average mechanical observable like the energy:

$$E_0(t) \equiv \sum_i p_i(t) E_{0i},$$

where $E_{0i}$ is the energy of the $i$-th microstate. The only difference is that the entropy is a thermodynamic quantity as an average of $-\eta(t)$. The index has its origin in the stochastic nature [16, 21, 22] of a statistical system. Thus, its nature is very different from the mechanical nature of observables like the energy, momentum, etc. although both averages...
give a statistical average. It is clear from Eq. (29) that the negative index $-\eta(t)$ is the contribution to the entropy from a single microstate. One may wish to think of $-\eta(t)$ as the entropy of a microstate, but this is not the conventional view as the entropy is an average quantity for the macrostate; see, however, Eq. (33). We refer the reader to recent reviews for more details [15, 16].

The probabilities $p_i(t)$ can be determined by considering an ensemble or by considering the temporal evolution, as described at length elsewhere [15, 16, 21, 22], but neither is really necessary provided the probabilities $p_i(t)$ are known. If it is known initially that $\Sigma_0$ is in some unique microstate $i_0$, then $p_i(0) \equiv \delta_{i,i_0}$ and $S_0(0) = 0$. As time goes on, and assuming that the dynamics is stochastic, the initial state will result in making various microstates available with some probabilities $p_i(t)$ at time $t$, and the entropy given by Eq. (29) will increase [32], until it reaches its maximum value. It is most certainly not a constant [16, 21, 22].

The time needed for all the microstates to be available is, in most cases, much shorter than the Poincaré recurrence time [15, 16, 21, 22]. It may indeed be smaller than the relaxation time $\tau_{\text{relax}}$. At the shorter time, all microstates have become available, but the entropy is still not necessarily at its maximum for the macrostate, since the microstates are not yet equiprobable. In the latter situation, the system is in internal equilibrium to be discussed below. If and only if all microstates are equally probable ($p_i(t) \to 1/W_0$ for all $i$), which happens after the relaxation time $\tau_{\text{relax}}$, do we have the maximum possible value of the entropy for the equilibrium macrostate:

$$S_0(t) \to S_{0,\text{eq}} \equiv \ln W_0 \quad \text{for } t \gtrsim \tau_{\text{relax}}. \quad (31)$$

This entropy is known as the Boltzmann entropy. It is the equilibrium value of the entropy and occurs because all microstates of the system are equiprobable. This entropy is constant in time and depends on the constant observables $E_0, V_0, N_0$, etc. The internal variables that are now constant are not independent of these observables in equilibrium [1, 2], so the entropy does not depend on them anymore.

It is possible in many cases that over a period of time smaller than $\tau_{\text{relax}}$, only a part of microstates, whose number is given by $W_0(t) < W_0$ have become available. In that case, the sum in Eq. (29) is restricted to $W_0(t)$. But the entropy is strictly less than $\ln W_0(t)$ unless all available microstates become equally probable. In that case, the entropy is given by

$$S_0(t) \to S_{0,\text{fin,eq}} \equiv \ln W_0(t) \quad \text{for } t < \tau_{\text{relax}}, \quad (32)$$

26
which is the Boltzmann entropy at that instance. This entropy is now a function of the internal variables, which themselves depend on time. However, $S_{0\text{in.eq}}(E_0, V_0, N_0, \xi_0(t))$ cannot have an explicit time-dependence as for fixed $E_0, V_0, N_0,$ and $\xi_0(t)$, $S_{0\text{in.eq}}(E_0, V_0, N_0, \xi_0(t))$ is its maximum possible value. This non-equilibrium state of the system with the entropy given by $S_{0\text{in.eq}}$ is said to be in internal equilibrium [1, 2], introduced in Sect. III.

The above discussion can be easily extended to an open system. It has already been shown [16] that the Gibbs entropy for the open system is given by exactly the same formula as Eq. (29) except that $i$ now represents one of the possible microstates of the open system $\Sigma$. Thus, everything said above applies to the entropy $S(t)$ of $\Sigma$ by removing the suffix 0 above. The only difference is that $E_0, V_0, N_0,$ etc. will be replaced by the instantaneous values $E(t), V(t), N$. The entropy $S_{\text{in.eq}}$ is a function of $E(t), V(t), \xi(t), N_0,$ etc. but it again cannot have an explicit dependence on time for the same reason that $S_{\text{in.eq}}$ is already maximum for fixed $E(t), V(t), \xi(t), N_0,$ etc. In the discussion below, we only consider the system $\Sigma$.

B. Importance of Equiprobable Microstates for Measurements and Microstate Entropy

The equiprobability assumption implies that the system exhibits no bias for any particular microstate, a point already emphasized by several authors in the past including Tolman [32, see Sect. 25, particularly, pp. 63-64], who uses this property of a statistical system as a postulate, when he discusses the validity of statistical mechanics. This postulate should be valid even for non-equilibrium states that appear in a system as we vary macroscopic conditions. This is the main idea about the internal equilibrium in our approach. The equiprobable or unbiased sampling assumption for the application of the two Boltzmann probabilities has a very important consequence for measurements in that one does not have to wait for the system to sample all of the relevant microstates. The latter is known to take astronomically large Poincaré recurrence time [21], as can be found in any decent textbook on statistical mechanics; see for example, Huang [29]. Let us consider a non-equilibrium system in internal equilibrium. Because of the equiprobable assumption,

$$p_i(t) = 1/W(t), \forall i,$$
where $W(t)$ denotes the number of microstates in the macrostate at that instant, so that the average of any thermodynamic quantity like the energy or entropy is given by

$$E(t) \equiv \sum_i E_i/W(t), \quad S(t) \equiv -\sum_i \eta_i/W(t) = -\eta,$$

in which the sum is over $W(t)$ microstates. In reality, equiprobable microstates do not have to imply an exact equiprobability; they can be within statistical error. One can think of $-\eta \equiv \ln W(t)$ as the entropy per microstate or the entropy of a microstate under the assumption of equiprobability. As the observables in each of these microstates take values within statistical fluctuations of the average observables, even a few samples will result in a highly reliable value of the observables. The only difference is that we need to replace $W(t)$ by the number of samples. This is what makes classical thermodynamics so reproducible within statistical fluctuations. For example, let us take a single sample, which happens to be in some microstate of energy $E$ with probability $1/W(t)$. The value of $E$ is within statistical error to the average energy $E(t)$. There is no sum in the definition for $E(t)$ now. The result is that

$$E(t) = E, \quad S(t) \equiv -\eta = \ln W(t). \quad (33)$$

A single sample, or equivalently a single microstate with probability $p(t) = 1/W(t)$, provides us with the energy $E$ within statistical error and with the Boltzmann entropy. The latter is not zero and contradicts the UCA Conjecture. The same is also true of other observables.

**Remark 10** There is no need to take the average over a large ensemble or over a long period of time.

This is why only a few samples to obtain average thermodynamic quantities give rise to highly reproducible results in thermodynamics. One most certainly does not have to take a very long time average or a very large ensemble average. The above discussion shows how the measurement will not affect the thermodynamic properties, in particular, the entropy of the system in accordance with the expectation noted in Sect. The requirement that the measurement should have ample time to sample all relevant microstates $W(t)$ is not only unnecessary but also not physical as that time is comparable to the Poincaré cycle. We believe that GMc have unnecessarily confused the issue by their following suggestion.
Consequently, only the time average can correctly reproduce the measured properties of glass. The underlying reason for this is that at any instant in time a system has one and only one representative point in phase space. The properties measured during a given experiment are a result of averaging over only those microstates that are accessed by the system during the measurement time. This, in a nutshell, is the principle of causality. For short observation times, only a small number of microstates are accessed. For long observation times, a large number of microstates are accessed.

Of course, it is possible in some rare cases that the sample we have is not a representative of internal equilibrium. In that case, we will obtain results that are not reproducible. But such a situation will be truly rare.

C. Gibbs vs Boltzmann Entropy Formulation

It should be clear from above that the Gibbs formulation is more general than the Boltzmann formulation \[15, 16, 21, 22\]. In both cases considered above, the Boltzmann entropy is the maximum possible entropy which occurs only when the available microstates have become equiprobable, and the system is either in equilibrium or in internal equilibrium \[1, 2\]. The system is said to be in equilibrium when Eq. \(31\) determines the entropy, and in internal equilibrium when Eq. \(32\) determines the entropy. In all other cases, the Gibbs entropy is the correct entropy of the system. As the Gibbs formulation supersedes the Boltzmann formulation, it seems to be the more general one to use for non-equilibrium systems. The relevance of the Gibbs formulation of entropy for non-equilibrium systems has been discussed recently \[15, 16, 21, 22\] by us, and we refer the reader to them for more details. We should, however, mention that Boltzmann’s \(H\)-theorem already shows that the Gibbs formulation is more general and conforms to the second law. We have also discussed \[15, 16\] there how the time-average is not very useful at low temperatures.

With the above discussion of the statistical entropy, we now turn to UCA. GMC \[11\] go on to state as a fact that “...the Gibbs entropy is valid for canonical systems in equilibrium,... cannot be used in nonequilibrium systems since it implicitly assumes ergodicity.” This is far from the truth; see above also. The Gibbs entropy is valid for any system (isolated or not), which need not be in equilibrium. We refer the reader to the derivation of the Gibbs
entropy formulation in Eq. (40.7) for a non-equilibrium ideal gas in the famous textbook by Landau and Lifshitz [30]; when this entropy is maximized, it gives the *grand canonical distribution*. But the point is that the Gibbs entropy is valid even for non-equilibrium systems. It also does not require ergodicity. It should be stressed that Gibbs never mentions ergodicity in his famous treatise [31]. The entropy of a non-equilibrium isolated system using Gibbs formulation is considered by Tolman [32] to show that it is a non-decreasing function of time and satisfies the second law. Using this formulation for the isolated system, it is easy to show [2, 15, 16] that the same formulation also applies to open systems. GMc use their above limited view of the Gibbs entropy to argue that the approach by Lebowitz and Goldstein of using the Boltzmann entropy formulation "... is the only one valid and consistent with the Second Law of nonequilibrium thermodynamics," see Claim 5. This is a very strong statement with the implication that it is the truth to be accepted by the reader. Unfortunately, the statement is not the truth as Gibbs formulation of the entropy also satisfies the second law as we have discussed above. Moreover, it is also not accepted by all workers in non-equilibrium thermodynamics. Even Ruelle [33], who is cited by GMc [11], categorically disagrees with the interpretation in UCA. We quote Ruelle [33]

"The fact that we take seriously the expression \( S(\rho) = -\int dx \rho(x) \ln \rho(x) \) for the entropy seems to be at variance with the point of view defended by Lebowitz, \( ^{20} \) who prefers to give physical meaning to a Boltzmann entropy different from \( S(\rho) \). There is, however, no necessary contradiction between the two points of view, which correspond to idealizations of different physical situations. Specifically, Lebowitz discusses the entropy of states which are locally close to equilibrium, while here we analyze entropy production for certain particular steady states (which maybe far from equilibrium)."

It is our opinion that GMc have unnecessarily confused the issue of the statistical interpretation of the entropy. While they argue for the superiority of the Boltzmann entropy for which no reasonable arguments are offered, they go back to use the Gibbs formulation, which they blame to be an equilibrium quantity, knowing well that the glass is not an equilibrium system. We find nothing wrong with the Gibbs formulation, contrary to the implications in UCA.

The suggestion by GMc that the glass confined to a component is like a canonical system
at fixed temperature and volume (while it is really a non-canonical system with time-varying
temperature and constant pressure) misses out the most important aspect of the glass transi-
tion. The temperature controlling the vibrations within the component and the temperature
describing component hopping over a longer period of time are two distinct temperatures.
As they do not include any internal variable in their approach, they miss out in capturing
all non-equilibrium contributions to the problem. All they seem to be concerned with is to
justify the loss of entropy using a computational approach. Proposing a computational ap-
proach that shows entropy of the glass below that of the supercooled liquid is not a proof of
the conjecture of the entropy loss. We need to ensure that the resulting physics is consistent
with the established laws of physics, such as the second law. We now turn to this aspect of
their approach.

D. Ergodicity and Causality

When the entropy is given by Eq. (31), the system is said to be ergodic. A system is
either ergodic or it is not. When the entropy is given by Eq. (32), one can say that the
system is ”ergodic with respect to the available microstates belonging to \( W(t) \).” But this is
not equivalent to the original concept of ergodicity, which is mathematically defined \([34–36]\)
by requiring the equality of infinite time and ensemble or phase-space averages; see also
Tolman \([32]\):

\[
\overline{f} = \langle f \rangle,
\]

where

\[
\overline{f} \equiv \lim_{t \to \infty} \frac{1}{t} \int_0^t f(t') \, dt', \quad \langle f \rangle \equiv \int f(p, q) \, dp\, dq / \int dp\, dq.
\]

The infinite-time average is required to ensure that the average does not depend on the
initial state of the system. Thus, the Deborah number

\[
D_e(t, \tau_{relax}) \equiv \frac{\tau_{relax}}{t} \overset{t \to \infty}{\to} 0
\]

if we wish to test whether a given system is ergodic or not. If we observe a system over a
period much shorter than \( \tau_{relax} \), so that \( D_e > > 1 \), all we observe is a non-equilibrium system,
but it tells us nothing about the system being ergodic or not. That can only be answered
by observing a system much much longer than \( \tau_{relax} \); indeed this time must be comparable
to the Poincaré cycle. Even if we observe the system for a period \( t \) comparable to \( \tau_{\text{relax}} \), the system has not have enough time to visit all relevant microstate. In this case,

\[
\bar{f}(t \sim \tau_{\text{relax}}) \equiv \frac{1}{t} \int_0^t f(t')dt'
\]

will be dominated by microstates that the system has visited during \( t \sim \tau_{\text{relax}} \); but these microstates have a strong correlation with the initial state, which may be far from equilibrium. Thus, such a finite time-average will not be equal to the ensemble average \( \langle f \rangle \) for the system, and one would incorrectly conclude that the system is non-ergodic, even if it is ergodic. It should be clear that because of the limit \( t \to \infty \), ergodicity is a property of an equilibrium state. It has no meaning for a non-equilibrium state. Therefore, any suggestion that a glass is non-ergodic requires the phenomenological assumption that it is a permanently frozen structure. This is most certainly not a valid assumption in the glass transition region. Thus, to speak of ergodicity breaking at or near \( T_{0g} \) is a misnomer in our opinion, even though it is loosely used in the literature.

In practical terms, a system is “ergodic” if, after sufficiently long time \( t \gg \tau_{\text{relax}} \), it visits all possible microstates consistent with a macrostate with equal probability. This is no different than the above mathematical definition, as the time required to visit all microstates is comparable to the Poincaré cycle \([15, 16, 21]\). However, the practical definition, which uses the macrostate, causes the following problem. It depends on how the macrostate is defined. As we have seen in Sect. III, the concept of a macrostate in non-equilibrium systems depends on time and will eventually become the equilibrium macrostate when \( t \approx \tau_{\text{relax}} \). This will make every system ergodic, whether the equilibrium state is unique or not, such as an Ising ferromagnet which has two distinct equilibrium states, and for which the macrostate can be described by the magnetization along with other observables. If, however, the magnetization is not used in specifying the macrostate, then the practical definition will show that the ergodicity is broken in ferromagnets. Usually, we require the equilibrium state to be not unique for the loss of ergodicity. Therefore, we believe that the mathematical definition of ergodicity as a limiting property is the proper way to investigate ergodicity. Such a definition will surely make the liquid above the melting temperature ergodic. Now, just because we observe an ergodic system such as this liquid at some time \( t < \tau_{\text{relax}} \), so that we observe a non-equilibrium state of the system, does not make the ergodic system non-ergodic. The system remains ergodic as it will eventually equilibrate to its unique equilibrium state for
\[ t \approx \tau_{\text{relax}} \] in accordance with its ergodic nature. Therefore, to speak of ergodicity restoration for a glass is not proper as the glass fully relaxes. From the proper mathematical definition of ergodicity, a glass is also "ergodic" as it will eventually equilibrate to the unique equilibrated supercooled liquid. The quotation marks on ergodic here is to reflect the fact that we are taking the corresponding crystal out of the consideration. These issues have been discussed elsewhere [15, 16].

Palmer [37] does talk about the loss of ergodicity, but it is understood that the relevant part of the phase space is a union of disjoint components with no possible transitions between them; the union of these components determine the macrostate. However, the system will be confined forever to one of these components, so that we can set \( \tau_{\text{relax}} \rightarrow \infty \) and \( D_e \rightarrow \infty \). The situation is similar to that in a ferromagnet, except that there are many more macrostates considered by Palmer. The ergodicity is clearly lost in this case. However, the situation with glasses is quite different since \( \tau_{\text{relax}} < \infty \) so that \( D_e \rightarrow 0 \) in the limit.

We believe that GMc unnecessarily complicate the issue of glass transition by invoking the loss of ergodicity just because we happen to observe the system in its non-equilibrium state at time intervals \( t < \tau_{\text{relax}} \). If we accept this rendition of ergodicity loss, even a liquid above its melting temperature will become non-ergodic at \( t < \tau_{\text{relax}} \), and no useful purpose is served by introducing such a concept of ergodicity. We refer the reader to a very good discussion of ergodicity by Tolman [32] and by Gallavotti [34, see, in particular, p. 257]. In our view, the glass transition at \( T_{0g} \) is a transition from equilibrated supercooled liquid to a non-equilibrium supercooled liquid and the transition at \( T_{0G} \) a transition from this non-equilibrium supercooled liquid to a glass, which is almost solid and its structure appears frozen over a long period of time \( (t \gg \tau_{\text{obs}}) \). Thus, our interpretation is different from GMc.

GMc also refer to the concept of causality in their work; see Conjecture [2]. This issue seems to be first raised by Kievelson and Reiss [38, 39]. It basically refers to the possible existence of a large number of degenerate microstates for a macrostate at absolute zero. According to Reiss [39]:

"Besides the residual entropy at 0 K being an artifact resulting from apparent entropy measurements along at least partially irreversible paths, this specification is incompatible with a view of the second law which establishes entropy as a
function of state. If it is a state function it depends only on its measured state, not upon the history of the system and certainly not upon its future. Since the system does not visit its alternative degenerate states during the time of measurement, it is unaware of these states, and the principle of causality forbids it to be affected by these states.”

The entropy in non-equilibrium thermodynamics is a generalized state function in that it is not only a function of instantaneous observables but also internal variables. The internal variables are no longer independent of the observables only when the system has come to equilibrium. Only the observables, and not the internal variables, are measurable. Thus, Reiss proposes a very narrow concept of entropy used in non-equilibrium thermodynamics. As the instantaneous observables and internal variables clearly depend on the history, Reiss’s assessment about the history dependence is incorrect. Moreover, as the second law destroys time-reversibility, the system is very much controlled by its ”future,” i.e. the equilibrium state. Every system, no matter how it is prepared, ”knows” exactly where its future lies and relaxes towards it. The idea of causality in the above quote with respect to the statistical entropy is somewhat misleading. Just as each role of a die results in an independent outcome, yet their probabilities are not independent (after all, they have to add to unity), different microstates are independent, yet their probabilities are not \[15, 16]. Let us clarify this by a simple example discussed by us elsewhere \[15, 16]. Let us throw an six-face unloaded die. Let the outcome of the throw be 5. Then, we have

\[ p_i = \delta_{i,5}, \quad i = 1, 2, \ldots, 6, \]

where \(\delta_{i,j}\) is the kronecker delta, and where \(i, j\) denote the six possible outcomes. Let us assume that the outcome of the next throw is 3. Then, \(p_5 = p_3 = 1/2\), and all other probabilities remain zero. Even if the two throws are independent, the probability distribution changes depending not only on the number of throws, but also on the particular outcomes. As the entropy is determined by the probability distribution, it should not come as surprise that the microstates (throws here), though independent, affect the value of the entropy. Only when the number of throws has become so large that \(p_i \to 1/6\), the ”equilibrium value,” can we say that additional throws will not affect the entropy. But this is precisely the property of an equilibrium state.
It should be clear that the probabilities of independent events are not independent in probability theory. As entropy is a statistical quantity (after all it is the average of the negative of the index $\eta$), its value is determined by microstate probabilities. Therefore, the entropy is a measure of the index of probability of all "independent" microstates. Causality has nothing to do with the concept of statistical entropy. Let us consider the case when microstates are equiprobable. The entropy of any sample at $t$ (a single microstate at that instance) is given by its probability, as shown in Eq. (33). Mechanical quantities such as energy, volume, etc. are not affected by this probability. The mechanical quantities are independent for each sample, as expected. But entropy, being a statistical or thermodynamic quantity, is determined by the probabilities, which themselves are controlled by the sum rule

$$\sum_i p_i(t) \equiv 1$$

over all microstates or samples, so that the probability is determined by the number of microstates $W(t)$. This expected result has nothing to do with the temperature such as the absolute zero and remains valid at all temperatures and at all times whenever internal equilibrium is present.

VI. LOSS OF ENTROPY IN UCA AND THE GLASS TRANSITION

Continuous vitrification results in the entropy curves (thermodynamic and statistical entropy $S(T_0, t)$ of Glass1 in CA and statistical entropy $\hat{S}(T_0, t)$ of Glass2 in UCA) in Fig. 2. Let us consider our system above $T_{0g}$, where the system is either the equilibrated supercooled liquid or the equilibrated liquid. Let $E', V'$ and $S'$ denote the energy, volume, and entropy of the equilibrated state at this temperature $T_0'$, respectively. The equilibrium value of the internal variable is denoted by $\xi'$. At time $t = 0$, we abruptly bring this system in contact with another medium at temperature $T_0$. Immediately prior to the instant the contact is made, the system is in some microstate $i'$, but we do not know precisely which microstate it is in. There is a probability $p_{i'}$ that the system is in microstate $i'$. Let $\tau$ denote the time required for $i'$ to evolve to another microstate at $T_0$. This microstate has no time to change immediately after the contact, so the system remains in the same microstate initially for $t < \tau$.

What is the entropy $S(T_0, t)$ for $t < \tau$ after the contact?
A. The Unconventional Approach

According to Conjecture 5, the statistical entropy \( \hat{S}(T_0, t) \) is identically zero (recall that we are considering the entropy and not just the configurational entropy here and in Fig. 2; similarly, our microstate refers to the system and not just to its configurational state):

\[
\hat{S}(T_0, t) \equiv 0 \text{ for } t < \tau.
\]

This will be true regardless of whether \( T_0 > T'_0 \) or \( T_0 < T'_0 \). We have already used this argument in Sect. 13 which we will now formalize. This zero entropy for \( t < \tau \) will result in an entropy curve similar to the entropy curve of Glass2 in Fig. 2 at \( T_0 \) in that it lies below \( S_{eq}(T_0) \), except that it is identically zero for \( t < \tau \). The argument works the same way even if \( T'_0 \) and \( T_0 \) happen to be above the melting temperature \( T_M \), where we have an ordinary liquid, which is not thought to lose ergodicity.

**Conclusion 11** It thus follows that the argument of the entropy loss in UCA has nothing to do with any impending glass transition or any impending loss of ergodicity, both of which require temperatures near \( T_{0G} \). It is merely a consequence of two distinct facts:

(a) the duration of observation \( \tau_{obs} < \tau \) (we will see below that this restriction on observation time is totally irrelevant for the conclusion);

(b) the entropy of a microstate is zero per Conjecture 6

Let us now consider the above thought experiment in time at any temperature \( T_0 \). The entropy is \( \hat{S}(T_0, t) \equiv 0 \text{ for } t < \tau \). We now watch the microstate \( i' \) to evolve to some other microstate \( i'^{(1)} \) at \( t = \tau \), and let \( \tau^{(1)} \) be the evolution time for \( i'^{(1)} \). Since the system is in a single microstate, it follows from Conjecture 3 that the entropy of the system is still zero for \( t < \tau + \tau^{(1)} \). We wait till \( t = \tau + \tau^{(1)} \) so that the current microstate evolves into another microstate \( i'^{(2)} \), and let \( \tau^{(2)} \) be the its evolution time. From the same reasoning, we find that

\[
\hat{S}(T_0, t) \equiv 0 \text{ for } t < \tau + \tau^{(1)} + \tau^{(2)}.
\]

It is easy to see that

\[
\hat{S}(T_0, t) \equiv 0 \text{ for } t \leq \infty.
\]

This makes the second part of Conjecture 3 inconsistent with its first part.
Conclusion 12  Conjecture 3 cannot be justified.

Even though we have rejected Conjecture 3, let us assume that the entropy $\hat{S}(T_0, t)$ continues to increase in time from its initial value $\hat{S}(T_0, 0) \equiv 0$ for reasons not clearly specified by GMc. We should recall, see Remark 4, that the statistical concept of entropy adopted by GMc cannot entertain the second law. So, its increase must be justified on some other grounds, which GMc have not done so far. Within the framework of the unconventional approach, let us ask: what would happen if $t = \tau_{\text{obs}}$? If the relaxation time $\tau_{\text{relax}} < \tau_{\text{obs}}$, the entropy $\hat{S}(T_0, t)$ will continue to increase and become equal to the equilibrium entropy. For $T_{0g} < T_0 < T_M$, the entropy will equal $S_{\text{eq}}(T_0)$ of the supercooled liquid. For $T_0 < T_{0g}$, $\hat{S}(T_0, t)$ will continue to increase from zero and become equal to the entropy $\hat{S}(T_0, \tau_{\text{obs}})$ of Glass2, see the horizontal bars on upward pointing arrows in Fig. 2 at $t = \tau_{\text{obs}}$ as it tries to grow to its equilibrium value $S_{\text{eq}}(T_0)$ for reasons not mentioned in UCA. If we disrupt the time-evolution at $t = \tau_{\text{obs}}$ such as by abruptly changing the temperature of the medium, the system will have this entropy $\hat{S}(T_0, \tau_{\text{obs}})$ at the moment the change is made. According to our understanding of UCA, this is the glass transition in the system. If we let the system relax at $T_0$, the entropy will continue to increase from $\hat{S}(T_0, \tau_{\text{obs}})$, this time from above the horizontal bar on the upwards arrow, until it reaches $S_{\text{eq}}(T_0)$ as $t \to \tau_{\text{relax}}(T_0)$. The entropy is always increasing, with the glass transition playing no special role in the growth of the entropy. We see no evidence of this process being inverse of the glass transition at $t = \tau_{\text{obs}}$; entropy $\hat{S}(T_0, t)$ is an increasing function of $t$ at all times:

Conclusion 13  We see no real difference in the way entropy behaves during the evolution of the system, which suggests that the glass transition and relaxation are not inverse processes.

B.  Entropy Loss and the Second Law

Regardless of the amount of drop (it does not even have to be comparable to $S_{\text{res}}$), the statistical entropy $\hat{S}(t)$ of such a non-equilibrium state in UCA must approach that of the supercooled liquid from below. This will result in the increase of the entropy during relaxation, which violates Eq. (22). As this equation was a consequence of the second law, we come to the following
Conclusion 14 A conjecture of entropy drop below that of the supercooled liquid will violate the second law as is clear from Eqs. (18), (21) and (22). Thus, the statistical entropy \( \hat{S}(T_0, t) \) and the thermodynamic entropy \( S(T_0, t) \) are two distinct quantities, with the statistical entropy \( \hat{S}(T_0, t) \) having no relevance to the glassy state.

C. Our Conventional Approach

We believe that the core of the problem with UCA is the conjecture about the entropy of a microstate; see Conjecture 3. The entropy is a property of a macrostate. However, if the system is in internal equilibrium or in equilibrium, then one can obtain the entropy of the system by simply using a microstate [21, 22], as seen in Eq. (33). This entropy is not always zero; it will be zero if and only if the microstate is unique. The macrostate corresponding to given \( E(t), V(t) \) and \( \xi(t) \) is the collection of all \( W(t) \) microstates with given \( E(t), V(t) \) and \( \xi(t) \) along with their probabilities [16]. All instantaneous thermodynamic averages including the instantaneous entropy are average quantities over the macrostate at that instant. Under the assumption of internal equilibrium, the instantaneous averages can be obtained from a single microstate or sample, as discussed in Sect. V B. The dynamics within a glass for it to jump from one microstate to another in time is not necessary for determining these instantaneous averages, an issue discussed elsewhere [15, 16] to which we refer the reader for details. When we pick a glass, or when we make an instantaneous measurement, we do not know which microstate it belongs to. All we know is the probability \( p_i \) for the microstate \( i \). If the glass formation occurs under an unbiased condition, all microstates will be equally probable so that

\[
p_i \equiv 1/W(t),
\]

and we obtain the Boltzmann entropy \( \ln W(t) \). Let \( W_G \) denote the number of possible microstates at absolute zero. When a glass is formed, it is equally likely to be in any of the \( W_G \) microstates at absolute zero so that the residual entropy resulting from this will be

\[
S_{\text{res}} = \ln W_G.
\]

The residual entropy will be zero if and only if we know for sure that the glass is a particular microstate, which will happen only if \( W_G \equiv 1 \). This we believe will represent an ideal glass. Just because one glass sample at absolute zero is in some microstate out of \( W_G \ (>1) \) does
not mean that the glass entropy is zero. The latter would be the case if we knew which particular microstate the glass sample happens to be. Only when \( W_G \equiv 1 \) can we be sure that all glass samples would be in the same microstate, and the glass entropy would be precisely zero \[16\]. In all other cases, all we know is that the probability that the system is in microstate \( i \) is \( p_i \), and the entropy is given by the Gibbs entropy in Eq. (29).

There is another way to understand this probability \[15, 16\]. We consider dividing the system into a large number of macroscopically large but quasi-independent parts of equal size, each of which can be in any microstate \( \iota \) associated with a part with a probability \( p_\iota \). Then the entropy \( s(t) \) of each part is given
\[
s(t) \equiv -\sum_\iota p_\iota(t) \ln p_\iota(t),
\]
and the entropy of the system, using its additive property, is given by
\[
S(t) = \sum s(t) \equiv N_P \overline{s}(t),
\]
where the sum is over all \( N_P \) parts of the system and \( \overline{s}(t) \) is the average entropy per part.

Once we recognize that the entropy of a microstate is in general not zero identically, we have no problem understanding that when we bring the system in contact with a medium at another temperature, the entropy immediately after the contact is also unchanged. It then changes towards the new equilibrium value during its relaxation, which is shown by downward arrows in Fig. 2. If we interrupt this relaxation at \( t = \tau_{\text{obs}} \) \( (T_0 < T_{0g}) \) by bringing the system in contact with a different medium at a lower temperature, the system will not completely relax. The current value of the entropy \( S(T_0, t = \tau_{\text{obs}}) \) becomes the initial value of the entropy at the new temperature. A sequence of such interruptions will eventually result in a ”frozen” glass below \( T_{0G} \). This understanding of the microstate entropy also shows that one does not have to observe the system over a period necessary to sample many of or all of the microstates associated with the macrostate or one does not require that the entropy is maximum only when all the microstates have been visited. The latter understanding of entropy has been criticized in the past by several authors; see for example Huang \[29\], Tolman \[32\], Gallovatti \[34\], Gujrati \[21\], and the argument has been revisited recently by Goldstein \[13\]: the time needed for all the microstates of a macroscopic system to be visited so that the entropy becomes maximum is beyond the current age of the universe. We have already argued against the time-average to be relevant for any measurement \[13, 16\]. In this
work, we have shown clearly that a single instantaneous measurement is sufficient to provide us with a thermodynamic description of the system at that instant. Any measurement that takes some finite non-zero duration will never yield any instantaneous information about the system.

VII. DISCUSSION AND CONCLUSIONS

We have briefly described and extended the conventional approach we have developed earlier for any non-equilibrium system. We consider the system $\Sigma$ to be surrounded by a very large medium $\tilde{\Sigma}$ to form the combined system $\Sigma_0$ so that the fields of the medium are not affected by the presence of processes going on inside the system, whatever they may. Thus, the approach can be applied to glasses; some authors sometimes identify them by some stretch of imagination as non-ergodic. However, whether ergodicity is lost or not plays no role in the behavior of the collection $\Sigma_0$, which we treat as an isolated body so that its thermodynamic entropy cannot decrease with time. This is the statement of the second law for the isolated body. We assume that both the body and the medium are separately in internal equilibrium, but not in equilibrium with each other. The internal equilibrium allows us to introduce instantaneous fields $T(t), P(t)$, etc. for the system and the constant fields $T_0, P_0$, etc. for the medium. We also use a single internal variable $\xi(t)$, in addition to $S(t), V(t)$ as induced internal variables, to describe possible relaxation in the system as it approaches equilibrium. The non-equilibrium nature of the system appears in the values of instantaneous fields $T(t), P(t)$, etc. being different from $T_0, P_0$, etc. of the medium. These differences in the fields cause non-negative irreversible entropy generation in accordance with the second law. In an isobaric vitrification, which is what we consider in this work, we assume that $P(t) = P_0$ at all times. The irreversible entropy generation requires $T(t) \geq T_0$; the equality occurs when there is equilibrium between the system and the medium. The instantaneous observables, internal variables and entropy at time $t$ are described by the microstate $i_t$ the system happens to be in at that instance along with its probability. This microstate also represents the instantaneous macrostate of the system. The effect of an instantaneous measurement is to give the values of the instantaneous observables and the entropy. The measurement does not alter the instantaneous value of the observables, internal variables, and the entropy. The entropy above refers to the thermodynamic entropy and
its statistical interpretation is obtained by the Gibbs entropy formulation: The *statistical entropy* is a statistical average of the negative index of microstate probabilities, just like the observables are of mechanical quantities. In our approach (CA), the two entropies behave in identical fashion. Any attempt to provide the classical entropy with a statistical interpretation must satisfy two important requirements:

CA1. It must decrease during relaxation in an isobaric vitrification process.

CA2. Its instantaneous value must not be affected by any instantaneous measurement.

In our approach, any non-equilibrium state, such as the one produced by changes in the medium by changing its temperature, relaxes towards its new equilibrium. During such a relaxation under isobaric cooling, the entropy, enthalpy and the instantaneous temperature decrease towards their respective equilibrium values. The relaxation is complete when we wait for \( t = \tau_{\text{relax}} \). During the relaxation process, the system will undergo a glass transition below \( T_{0g} \); if the system is abruptly changed at \( t = \tau_{\text{obs}} < \tau_{\text{relax}} \) by bringing it in contact with a medium at a lower temperature. The *instantaneous macrostate* of the system, described in terms of its observables and internal variable, does not change when the contact is made. This also means that the entropy also does not change. If the contact is not made, the relaxation will continue to go on. Thus, the glass transition and relaxation are part of the same relaxation process in CA. There is nothing inverse about them. The gain in the thermodynamic entropy of the medium is shown to be bounded from above by the maximum change \( \Delta S_{\text{eq}}(T_0) \); the latter is the maximum possible decrease in the thermodynamic entropy of the system. From a careful analysis, we have concluded that the thermodynamic entropy \( S(T_0, t) \) of the system, such as Glass1, must always be above \( S_{\text{eq}}(T_0) \); thus, the thermodynamic entropy must decrease during relaxation; the decrease is a consequence of the second law.

The conclusion of the thermodynamic approach is summarized in Theorem \( \Box \) the thermodynamic entropy must decrease with time during any isothermal relaxation in isobaric vitrification.

UCA developed by GMc as an attempt to describe glass transition in any material does not fulfill both requirements CA1 and CA2. Not only that, the glass transition and relaxation are described as inverse processes. Faced with these discrepancies and several other
unconventional and not adequately explained aspects of UCA, we have carefully examined it in this work. To test the validity of their inverse conjecture UCA5, we decided to treat $\Sigma$ as part of $\Sigma_0$. We do this to determine the entropy gain by the medium to show unambiguously whether the system can lose so much entropy at the glass transition that it lies below $S_{eq}$ in Fig. 2; see UCA5.

GMc incorrectly conclude that the use of classical thermodynamics to calculate the thermodynamic entropy is logically inconsistent (UCA1). Using this erroneous conclusion they argue that the residual entropy must vanish in accordance with the third law (UCA2). However, a careful reconsideration shows that there is nothing wrong in using the classical non-equilibrium thermodynamics. Indeed, its use clearly establishes that the calorimetric entropy $S_{\text{expt}}(0)$ at absolute zero is a *lower bound to the residual entropy*; the former entropy is normally found to be non-negative, which makes

$$S_{\text{res}} \geq S_{\text{expt}}(0) > 0.$$  

Thus, the primary motivation of GMc to develop their unconventional approach UCA is based on an incorrect understanding of classical thermodynamics.

As discussed in Sect. II, UCA is based on a set of conjectures, some of which are interrelated, left unproven or satisfactorily justified by GMc. In particular, as summarized in Remark 4 their statistical formulation $\hat{S}(T_0, t)$ of the entropy, which is based on the zero-entropy conjecture UCA3 for a microstate, has nothing to do with the thermodynamic entropy $S(T_0, t)$ used in the second law in Eq. (1). The entire UCA is based solely on this statistical notion of entropy and its computation. This formulation of $\hat{S}(T_0, t)$ in UCA has been developed with a goal to show entropy loss; yet we find that this formalism, in particular the growth of the statistical entropy with time in Conjecture 3, is *inconsistent* with UCA3; the latter, if accepted, only results in $\hat{S}(T_0, t) = 0$ at all times under all conditions including all temperatures. *This is most certainly unphysical.* In our opinion, it is this conjecture that results in the entropy loss during a glass transition under cooling.

Even if we allow for the entropy to increase from zero due to some unknown reasons, not offered by GMc, we find that $\hat{S}(T_0, t)$ will always increase towards $S_{eq}(T_0)$ of the equilibrated supercooled liquid. We find no justification that the relaxation and glass formation are inverse processes. Their statistical entropy $\hat{S}(T_0, t)$ increases in both processes. The increase of entropy scenario would hold at all temperatures, not just at and below $T_{0g}$. Thus, the
entropy loss conjecture has nothing to do with any glass transition or any ergodicity loss; it is merely a consequence of the zero-entropy conjecture UCA3. The increase of the statistical entropy $\hat{S}(T_0, t)$ in UCA contradicts the decrease of the thermodynamic entropy found in CA. Thus, the statistical entropy in UCA cannot represent the thermodynamic entropy of a glass. As their computation also shows an increase of their statistical entropy, their computational scheme is not useful to understand glasses.

The statistical entropy due to Gibbs that is used in CA remains in conformity with the behavior of the thermodynamic entropy. The entropy of a microstate, see Eq. (33), is not necessarily zero. Thus, at each instant of time, the entropy of a system, which happens to be in a microstate, is not zero in CA. This instantaneous entropy for an isolated system will always increase, but for an open system such as a glass may decrease. The latter behavior is in accordance with the second law. In both cases, it is the irreversible entropy generation that can never be negative. It is our belief that GMc have overlooked this distinction between the entropy and irreversible entropy generation in their approach, which causes them to incorrectly believe that the entropy must increase during isothermal relaxation in vitrification.

It is our opinion that GMc have unnecessarily confused the issue of the statistical concept of entropy by implying that the Gibbs entropy is not suitable to describe glasses but the Boltzmann entropy is. This is not a correct conclusion. Both formulations are appropriate, but care must be exercised to interpret them properly. Let us assume equiprobability of microstates. The number of relevant microstates $W(t)$ is most certainly not the number of microstates sampled by any measurement for a macrostate in time, as GMc suggest. The time for that is of the order of Poincaré cycle and far exceeds the age of the universe. It is really the number of microstates available to the system, as explained earlier, and even an instantaneous measurement will give the expected value of the observables. This is what makes thermodynamics so reliable a science. This interpretation is the same whether we use the Gibbs entropy formulation or the Boltzmann entropy formulation. There is no difference between them as long as we deal with internal equilibrium. Their continuous assertion in various publication that they are different is most probably due to their misunderstanding, and serves no purpose except to confuse the issue of the statistical entropy. There is no reason at all to doubt that the thermodynamic and statistical entropies are different in any way.
It is our opinion that they have also unnecessarily made too much of an issue of ergodicity loss and of causality in glasses. All one needs to do is to treat glasses as a non-equilibrium state and to recall that the statistical entropy is an average of a statistical quantity, the negative index of probability as discussed in the work. GMc have taken a very simplistic view of glasses by ignoring internal variables, two-temperature description and the fact that fluctuation-dissipation theorems used by them [11] fail for glasses.

We finally conclude that their current theoretical and computational attempts using UCA has no relevance for glasses.

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