Some Rigorous Results Relating Nonequilibrium, Equilibrium, Calorimetrically Measured and Residual Entropies during Cooling

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(Dated: May 11, 2014)

Abstract

We use rigorous nonequilibrium thermodynamic arguments to establish that (i) the nonequilibrium entropy \(S(T_0)\) of any system is bounded below by the experimentally (calorimetrically) determined entropy \(S_{\text{expt}}(T_0)\), (ii) \(S_{\text{expt}}(T_0)\) is bounded below by the equilibrium or stationary state (such as the supercooled liquid) entropy \(S_{\text{SCL}}(T_0)\) and consequently (iii) \(S(T_0)\) cannot drop below \(S_{\text{SCL}}(T_0)\). It then follows that the residual entropy \(S_R\) is bounded below by the extrapolated \(S_{\text{expt}}(0) > S_{\text{SCL}}(0)\) at absolute zero. These results are very general and applicable to all nonequilibrium systems regardless of how far they are from their stationary states.

I. INTRODUCTION

Nonequilibrium states like glasses from supercooled liquids (SCLs) are abundant in Nature, whose entropy \(S\) can only be estimated by calorimetrically measured entropy \(S_{\text{expt}}\), which can then be extrapolated to absolute zero. The extrapolated value \(S_R\) at absolute zero is commonly known as the \textit{residual entropy} and is normally found to satisfy \(S_R > 0\). In practice, one considers the isobaric entropy \(S(T_0)\) of the system as a function of the temperature \(T_0\) of the surrounding medium; see Fig. 1. The existence of \(S_R\) was first theoretically demonstrated by Pauling and Tolman \[1\]; see also Tolman \[2\]. In addition, the existence of the residual entropy has been demonstrated rigorously for a very general spin model by Chow and Wu \[3\]. The residual entropy for glycerol was observed by Gibson and Giauque \[4\] and for ice by Giauque and Ashley \[5\]. Pauling \[6\] provided the first numerical estimate for the residual entropy for ice, which was later improved by Nagle \[7\]. Nagle’s numerical estimate has been recently verified by simulation \[8, 9\]. The numerical simulation carried out by Bowles and Speedy \[10\] for glassy dimers also supports the existence of a residual entropy. For a brief review of the history of the residual entropy, see \[11–18\]. Thus, it appears that the support in favor of the residual entropy, see the curve Glass1 in Fig. 2, is quite strong. Its existence also does not violate Nernst’s postulate, as the latter is applicable only to true equilibrium states with a \textit{non-degenerate} ground state \[19–21\]. Indeed, many exactly solved statistical mechanical models show a non-zero entropy at absolute zero. However, as of yet, no experiment can be performed at absolute zero to experimentally determine the residual entropy; in all cases, some sort of \textit{extrapolation} is required. This point should not be forgotten in the following whenever we speak of the residual entropy. Despite the above mentioned support for the reality of the residual entropy, it has become a highly debated issue in the literature \[22–28\] as discussed by these authors. The reason for the debate is that the relationship among \(S(T_0)\), \(S_{\text{expt}}(T_0)\) and the entropy \(S_{\text{SCL}}(T_0)\) of the corresponding stationary state is not well understood, and understanding this relationship is the main theme of this work.

In the following, we will speak of "the equilibrium" state associated with a nonequilibrium state as the stationary (time-independent) state. Depending on the context, the equilibrium state may represent a true equilibrium state such as a crystal or a stationary metastable state such as the supercooled liquid. A nonequilibrium state in this work will always be taken as a system in its stationary state.

FIG. 1: An isolated system \(\Sigma_0\) consisting of the system \(\Sigma\) in a surrounding medium \(\Sigma\). The medium and the system are characterized by their fields \(T_0\), \(P_0\), and \(T(t), P(t)\), respectively, which are different when the two are out of equilibrium.
rate of cooling so that the glass is a nonequilibrium state \cite{31,32}. As the irreversibility due to the glass transition does not allow for an exact evaluation of the entropy, it has been suggested \cite{27,28} that the entropy decreases by an amount almost equal to \( S_R \) within the glass transition region so that the glass (see Glass2 in Fig. 2) whose entropy lies below the supercooled liquid) would have a vanishing entropy at absolute zero. It has been shown by Goldstein \cite{11} that Glass2 results in a violation of the second law. It should be stressed that if there is ever any conflict between the second law \cite{33} and any other law in physics such as the zeroth or the third law, it is the second law that is believed to hold in all cases. One can also argue that to confine the glass into a unique basin in the energy landscape requires microscopic information \cite{15,32,34}; hence, the particular glass cannot be considered in a macrostate. Oppenheim \cite{35} has also raised somewhat of a similar objection.

We have drawn the two entropy curves (Glass1 or Glass2) in Fig. 2 that emerge out of the entropy curve for the equilibrated supercooled liquid for a given \( \tau_{\text{obs}} \) in such a way that Glass1 has its entropy above (so that \( S_R \gtrless 0 \)) and Glass2 below (so that \( S_R = 0 \)) of the supercooled liquid. The entropy of Glass1 (Glass2) approaches that of the equilibrated supercooled liquid entropy from above (below) during isothermal (fixed temperature of the medium) relaxation; see the two downward vertical arrows for Glass1. It is the approach to equilibrium that distinguishes the two glasses, Glass1 and Glass2. Almost all experimental investigations leave open the possibility that Glass2 may materialize if the irreversibility is too large. Our work clarifies the situation.

It is abundantly clear from the above discussion that there is a need to look at the relationship between various entropies in Fig. 2. As is customary, we treat the supercooled liquid as an equilibrium state, even though it is not a true equilibrium state; see above. We proceed by following the strict second law inequality \( dS > 0 \)\cite{29,30,36,37}, see Eq. (1), and use it to prove the following results applicable to all nonequilibrium systems, regardless of how close or far they are from their equilibrium state:

1. Various entropies obey the following strict inequalities
\
\[ S(T_0) > S_{\text{expt}}(T_0) > S_{\text{SCL}}(T_0) \quad \text{for} \quad T_0 < T_{0g} , \]

so that the entropy variation in time has a unique direction as shown by the downward arrows in Fig. 2. Thus, \( S(T_0) \) cannot drop below \( S_{\text{SCL}}(T_0) \) (such as Glass2 in Fig. 2) without violating the second law \cite{33}.

2. The experimentally observed non-zero entropy at absolute zero in a vitrification process is a strict lower bound of the residual entropy of any system:
\
\[ S_R \equiv S(0) > S_{\text{expt}}(0) > S_{\text{SCL}}(0) . \]  

\section{II. Entropy Bounds During Vitrification}

The Eq. (1) is consistent with Glass1 but not with Glass2. All experiments on or exact/approximate computations for nonequilibrium systems must obey the strict inequalities in Eqs. (1) without exception. This is the meaning behind the usage of “... rigorous ...” in the title. The actual values of the entropy are not relevant for the aim of this work, which is to find the relationship among different entropies under vitrification. Because of the possibility that the systems may be far away from equilibrium such as in a fast quench, where the irreversible contributions may not be neglected, our results go beyond the previous calorimetric evidence \cite{12,13,18,23}. The systems we are interested in include glasses and imperfect crystals as special cases. However, to be specific, we will only consider glasses below.
temperature $T_{0G}$ (not too far from $T_{0g}$) to form an amorphous solid with a viscosity close to $10^{13}$ poise. This solid is identified as a glass. The location of both temperatures depends on the rate of cooling, i.e. on $\tau_{\text{obs}}$. Over the glass transition region between $T_{0G}$ and $T_{0g}$ in Fig. 2 the system gradually turns from an equilibrium supercooled liquid at or above $T_{0G}$ into a glass at or below $T_{0g}$\cite{31, 32, 38}. We overlook the possibility of the supercooled liquid ending in a spinodal\cite{39}. It is commonly believed that $S_{\text{SCL}}(0)$ will vanish at absolute zero ($S_{\text{SCL}}(0) = 0$), as shown in the figure. However, it should be emphasized that the actual value of $S_{\text{SCL}}(0)$ has no relevance for the theorems below.

We will only consider isobaric cooling (we will not explicitly exhibit the pressure in this section), which is the most important situation for glasses. The process is carried out along some path from an initial state $A$ at temperature $T_0$ in the supercooled liquid state which is still higher than $T_{0g}$ to the state $A_0$ at absolute zero. The state $A_0$ depends on the path $A \rightarrow A_0$ which is implicit in the following. The change $dS$ between two neighboring points along such a path is $dS = d_eS + d_iS$ in modern notation \cite{29, 30, 36, 37, 40, 41}. The component

$$d_eS(t) = d_eQ(t)/T_0 = C_PdT_0/T_0$$

represents the reversible entropy exchange with the medium in terms of the change in heat $d_eQ(t)$ (in keeping with the modern notation) added to the glass by the medium at time $t$ to the medium at $T_0$ and the heat capacity $C_P$. It also represents the calorimetrically determined change in the entropy in any process. The component

$$d_iS > 0$$

represents the irreversible entropy generation within the system in the irreversible process, and contains, in addition to the contribution from the irreversible heat transfer with the medium, contributions from all sorts of viscous dissipation going on within the system and normally require the use of internal variables \cite{29, 30, 36, 40, 41}. The equality in Eq. 4 holds for a reversible process, which we will no longer consider unless stated otherwise. A discontinuous change in the entropy is ruled out from the continuity of the Gibbs free energy $G$ and the enthalpy $H$ in vitrification proved elsewhere \cite{29}. Thus, we only consider a continuous change in the entropy as shown by the two glass curves in Fig. 2.

**Theorem 1** The experimentally observed (extrapolated) non-zero entropy at absolute zero in a vitrification process is a strict lower bound of the residual entropy of any system:

$$S_R \equiv S(0) > S_{\text{expt}}(0).$$

**Proof.** We have along $A \rightarrow A_0$

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

where we have assumed that there is no latent heat in the vitrification process. Since the second integral is always positive, and since the residual entropy $S_R$ is, by definition, the entropy $S(0)$ at absolute zero, we obtain the important result

$$S_R \equiv S(0) > S_{\text{expt}}(0) \equiv S(T_0) + \int_0^{T_0} C_P dT_0/T_0. \tag{6}$$

This proves Theorem 1. The integral represents the calorimetric contribution.

The strict forward inequality above clearly establishes that the residual entropy at absolute zero must be strictly larger than $S_{\text{expt}}(0)$ in any nonequilibrium process.

**Theorem 2** The calorimetrically measured (extrapolated) entropy during processes that occur when $\tau_{\text{obs}} < \tau_{\text{relax}}(T_0)$ for any $T_0 < T_{0g}$ is larger than the supercooled liquid entropy at absolutely zero

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

**Proof.** Let $Q_e(t) \equiv d_eQ(t)/dt$ be the rate of net heat loss by the system. For each temperature interval $dT_0 < 0$ below $T_{0g}$, we have

$$|d_eQ| = C_P \left| dT_0 \right| = \int_0^{T_0} \left| Q_e \right| dt < \left| dQ_{\text{eq}} \right| \quad T_0 < T_{0g}$$

where $\left| dQ_{\text{eq}} \right| (T_0)$ denotes the net heat loss by the system to come to equilibrium, i.e. become supercooled liquid during cooling at $T_0$. For $T_0 \geq T_{0g}$, $d_eQ = d_eQ_{\text{eq}}(T_0) = C_{P_{\text{eq}}}dT_0$. Thus,

$$\int_0^{T_0} C_P dT_0/T_0 > \int_0^{T_0} C_{P_{\text{eq}}}dT_0/T_0.$$

We thus conclude that

$$S_{\text{expt}}(0) > S_{\text{SCL}}(0). \tag{7}$$

This proves Theorem 2.

The strict inequalities above are the result of glass being a nonequilibrium state. We have now verified the second statement in the Introduction.

The difference $S_R - S_{\text{expt}}(0)$ would be larger, more irreversible the process is. The quantity $S_{\text{expt}}(0)$ can be determined calorimetrically by performing a cooling experiment. We take $T_0$ to be the melting temperature $T_{0M}$, and uniquely determine the entropy of the supercooled liquid at $T_{0M}$ by adding the entropy of melting to the crystal entropy $S_{CR}(T_{0M})$ at $T_{0M}$. The latter is obtained in a unique manner by integration along a reversible path from $T_0 = 0$ to $T_0 = T_{0M}$:

$$S_{CR}(T_{0M}) = S_{CR}(0) + \int_0^{T_{0M}} C_P_{CR}dT_0/T_0,$$
here, $S_{CR}(0)$ is the entropy of the crystal at absolute zero, which is traditionally taken to be zero in accordance with the third law, and $C_{P,CR}(T_0)$ is the isobaric heat capacity of the crystal. This then uniquely determines the entropy of the liquid to be used in the right hand side in Eq. (3). We will assume that $S_{CR}(0) = 0$. Thus, the experimental determination of $S_{\text{expt}}(0)$ is required to give the lower bound to the residual entropy in Eq. (2).

Experiment evidence for a non-zero value of $S_{\text{expt}}(0)$ gives a value of $S_{\text{expt}}(0)$ above a mathematical justification of the value of its entropy at zero, which is traditionally taken to be zero in accordance with the third law, and $C_{P,CR}(T_0)$.

We have proved Theorems 1 and 2 by considering only the system without paying any attention to the medium. For Theorem 1 we require the second law, i.e. Eq. (4). This is also true of Eq. (8). The proof of Theorem 2 requires the constraint $\tau_{\text{abs}} < \tau_{\text{rel}}(T_0)$ for any $T_0 < T_{0g}$, which leads to a nonequilibrium state. The same is also true of Eq. (10).

### III. CONCLUSIONS

We have considered the role of irreversible entropy generation during isobaric vitrification to rigorously justify the two statements in the Introduction. They are valid regardless of how far the system is out of equilibrium. Thus, our results are very general and are not restricted by the small amount of irreversibility that is normally considered in the literature. The first statement shows that the instantaneous entropy $S(T_0, t)$ must always be higher than $S_{\text{expt}}(T_0)$, which in turn must always be higher than $S_{\text{SCL}}(T_0)$ of the equilibrated supercooled entropy. The second statement shows that the extrapolation of the calorimetrically measured entropy to absolute zero forms a strict lower bound to the residual entropy $S_R$. As the former is usually positive, this proves that the residual entropy has to be at least as large as this value. From the first statement, it also follows that Glass2 is not realistic.

The statements follow from considering the thermodynamic entropy that appears in the second law, and their validity is not affected by which equivalent statistical definition of entropy one may wish to use for the thermodynamic entropy, an issue that has been investigated by us recently [37].

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By the second law we mean the law of increase of the entropy according to which the (thermodynamic) entropy of an isolated system can never decrease. Any statistical interpretation of this law must ensure this law.

The preparation to get the system in a unique microstate requires knowing precisely the cell $C_i$ a particular particle $i$ belongs to. This should be contrasted with the situation such as in a crystal or a glass, in which, although each particle is confined within a cell, we have no knowledge which particle belongs to this cell. This ambiguity in the microstates is a characteristic of a statistical system[14, 15] that results in a macrostate. The preparation of a unique microstate results in a unique specification and is not physically feasible to accomplish in reality.

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