Comment on ”Comment on: On the reality of residual entropies of glasses and disordered crystals” [J. Chem. Phys. 129, 067101 (2008)]

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Abstract

By using very general arguments, we show that the entropy loss conjecture at the glass transition violates the second law of thermodynamics and must be rejected.
Gupta and Mauro\textsuperscript{1} in their comment on a recent paper by Goldstein\textsuperscript{2} explain their entropy loss conjecture (ELC) as follows: when a glass (GL) is held at a fixed temperature for a period longer than the experimental time scale $\tau$ used for its preparation, it tends spontaneously towards the equilibrium state of the supercooled liquid (SCL), the process known as the structural relaxation. They also claim that the configurational entropy increases during this relaxation process. This they say follows from the process being spontaneous and the second law, the law of increase of entropy: see the figure in their paper\textsuperscript{1}. They also identify the glass transition as the inverse of relaxation. Hence, they claim that the configurational entropy $S^{(c)}$ must decrease during the glass transition. This seems to be their justification of ELC. The situation with a discontinuous entropy loss is schematically shown in Fig. 1, where the blue curves show the entropies of SCL and the GL, and the dashed green vertical jump shows the discontinuity of magnitude $S_R$ at the glass transition at $T_g$. For a finite system such as those investigated in simulations, this discontinuity most probably will be replaced by a continuous piece shown by the dashed red curve.

It is agreed by all, and this is also supported by experiments, that the enthalpy $H$ and the volume $V$ show no discontinuity at the glass transition. Consequently, the entropy discontinuity gives rise to a discontinuous jump in the Gibbs free energy $G = H - TS$ in the amount of $T_gS_R$, as shown by the blue curves and the green discontinuity in Fig. 2. The red curve shows the Gibbs free energy when the entropy loss in Fig. 1 is continuous. We will discuss the continuous behavior later. For the moment, we are interested in the discontinuity behavior of ELC discussed by Gupta and Mauro\textsuperscript{1}.

Goldstein\textsuperscript{2} had used some plausible assumptions and Henry’s law to argue that ELC would lead to the violation of the second law. Gupta and Mauro\textsuperscript{1} countered by claiming that the glass transition is not a spontaneous process, so the discontinuous drop in its entropy is not a violation of the second law. Which claim is right? How should we resolve this impasse? Any attempt to resolve the issue must be based on some general arguments which not only bypasses the limitations of the arguments used by Goldstein, but also bypasses any assumption of whether the glass transition is spontaneous or not. In this comment, we establish on very general grounds that the above discontinuity in the Gibbs free energy violates the second law. As this discontinuity is a consequence of ELC, ELC itself cannot be valid.

The glass is a system far from equilibrium so one may not apply equilibrium statistical
mechanics or equilibrium thermodynamics to investigate its properties, which vary with time. One may resort to apply non-equilibrium thermodynamics, not a well-developed field at present, to study glasses and their relaxation in time. To avoid discussing whether the glass transition is a spontaneous process or not, we consider an isolated system Σ₀ composed of the system Σ of interest (GL/SCL) in a medium denoted by Ŝ. We also do not commit as to how the entropy is calculated in order to avoid the contentious debate about which formalism is the correct one, except to demand that the formalism is equally applicable to SCL and GL, and that it satisfies the second law. We then follow the consequences of the second law applied to the isolated system. We will consider a single component system, which is sufficient for our purpose. According to this law, the entropy $S₀(t)$ of an isolated system $Σ₀$ can never decrease in time. In general, $S₀$ also depends on the number of particles $N₀$, energy $E₀$, and volume $V₀$ of $Σ₀$. Thus, $S₀(t)$ used above should be really written as $S₀(E₀,V₀,N₀,t)$. However, as the extensive quantities remain constant in time there is no harm in using the compact form $S₀(t)$ during approach to equilibrium. The energy, volume and the number of particles of $Σ$ are denoted by $E$, $V$, and $N$, respectively, while that of the medium $Ŝ$ by $Ê$, $Ṽ$, and $Ñ$. Obviously,

$$E₀ = E + Ê, \quad V₀ = V + ÊV, \quad N₀ = N + Ñ.$$
FIG. 2: Schematic form of the concave free energy $G$ as a function of the temperature $T$. The blue curve represents the Gibbs free energy for a macroscopically large system; the green discontinuity $T_gS_R$ at $T_g$ shown by the broken green portion corresponds to the residual entropy loss $S_R$. (This discontinuity will be absent if there were no entropy loss.) For finite systems, this discontinuity will be most probably replaced by a continuous curve shown by red, which can be conveniently divided into three different pieces: the two solid red pieces connected by a dot-dashed piece with an inflection point A. This continuous curve has a region of negative heat capacity, making it unphysical.

We will assume that $N$ of the system is also fixed, which means that $\tilde{N}$ is also fixed. However, the energy and volume of the system may change with $t$.

When the isolated system is in equilibrium, its entropy $S_0(E_0, V_0, N_0, t)$ has reached its maximum and no longer has any explicit time-dependence so that it can be simply written as $S_0(E_0, V_0, N_0)$ or $S_0$. In this case, different parts of $\Sigma_0$ have the same temperature $T = (\partial E_0/\partial S_0)$ and pressure $P = T(\partial V_0/\partial S_0)$. Otherwise, the entropy $S_0(t)$ continuously increases and the isolated system is said to be not in equilibrium. The medium is considered to be very large compared to $\Sigma$, so that its temperature, pressure, etc. are not affected by the system. We assume $\Sigma$ to be in internal equilibrium (its different parts have the same temperature and pressure, but $\Sigma$ and $\Sigma$ may not be in equilibrium with each other). Thus,
its entropy no longer has an explicit time dependence, but has implicit $t$-dependence through the $t$-dependence of $\tilde{E}$, and $\tilde{V}$. Below the glass transition at $T_g$, GL ($\Sigma$) will relax so as to come to equilibrium with the medium if we wait longer than $\tau$.

The entropy $S_0$ of the isolated system can be written as the sum of the entropies $S$ of the system and $\tilde{S}$ of the medium:

$$S_0(E_0, V_0, N_0, t) = S(E, V, N, t) + \tilde{S}(\tilde{E}, \tilde{V}, \tilde{N});$$

there is no explicit $t$-dependence in $\tilde{S}(\tilde{E}, \tilde{V}, \tilde{N})$ due to internal equilibrium. The correction to this entropy due to the weak stochastic interactions between the system and the medium has been neglected, which is a common practice. We expand $S_0$ in terms of the small quantities of the system

$$\tilde{S}(\tilde{E}, \tilde{V}, \tilde{N}) \simeq \tilde{S}(E_0, V_0, \tilde{N}) - \left( \frac{\partial \tilde{S}}{\partial \tilde{E}} \right)_{E_0} E(t) - \left( \frac{\partial \tilde{S}}{\partial \tilde{V}} \right)_{V_0} V(t).$$

It follows from the internal equilibrium of $\tilde{\Sigma}$ that

$$\left( \frac{\partial \tilde{S}}{\partial \tilde{E}} \right)_{E_0} = \frac{1}{T}, \quad \left( \frac{\partial \tilde{S}}{\partial \tilde{V}} \right)_{V_0} = \frac{P}{T},$$

and $\tilde{S} \equiv \tilde{S}(E_0, V_0, \tilde{N})$, which is a constant, is independent of the system. Thus,

$$S_0(t) - \tilde{S} \simeq S(E, V, N, t) - E(t)/T - PV(t)/T.$$

Let us introduce

$$G(t) \equiv H(t) - TS(t), \quad H(t) \equiv E(t) + PV(t),$$

the time-dependent Gibbs free energy and enthalpy of the system $\Sigma$ with the medium $\tilde{\Sigma}$ at fixed $T$ and $P$. In terms of these functions, we have

$$S_0(t) - \tilde{S} = S(t) - H/T = -G/T.$$

In deriving the above equation, no assumption about the system $\Sigma$ has been made. In particular, we have not assumed any particular aspect of its non-equilibrium nature. We have also not assumed whether the glass transition is spontaneous or not. The identification of $S_0(t) - \tilde{S}$ with the Gibbs free energy of $\Sigma$ is generally valid under the assumption of the
medium being large compared to Σ, which can be satisfied as well as we wish. Now, if $G$ underwent a discontinuous jump upwards as SCL turns into GL at the glass transition in a cooling experiment, see Fig. 2 it will lower the entropy of the isolated system by $S_R$. But, this is inconsistent with the second law! Therefore, there cannot be an entropy loss in the system as SCL turns into GL at the glass transition. This proves our above claim.

The above violation of the second law occurs because of the discontinuity. The violation will not occur if the jump is replaced by a continuous patch as shown in Figs. 1 and 2. Now, the Gibbs free energy must be a concave function of the temperature so that the heat capacity remains non-negative, as the blue curves are in Fig. 2. The free energy must always curve downwards for $C_P$ to remain non-negative. The red curve contains three different pieces: the two solid pieces in Fig. 2 on either side of the dot-dashed piece in the middle containing an inflection point A where the curvature changes its sign. The solid pieces are concave as required by stability. But it is also clear that any attempt to smoothly connect the two solid pieces by the dot-dashed piece near $T_g$ must result in the middle piece, which cannot remain concave everywhere. It must have a convex piece at higher temperatures, which will then result in a region of negative heat capacity as shown by the arrow, and which will make the system unphysical. Recently, Mauro et al. have reported model computation results for a finite system of selenium by using several cooling rates. They observe a continuous drop in the configurational entropy. Unfortunately they have not carried out any finite size analysis, so it is not possible to know what happens to the continuous drop in the limit of a macroscopically large system. They have also not reported the heat capacity or the entropy so no comment can be made regarding their behavior. We will have to wait for their answer.

1 P.K. Gupta and J.C. Mauro, J. Chem. Phys. 129, 067101 (2008).
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