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On resolving the statistical and calorimetric entropies of glass and non-crystalline solids, and the residual entropy problem

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ABSTRACT

In statistical terms, the configurational entropy, S_{conf}, of a structure of fixed configuration is zero, i.e., its $\Omega = 1$ in the Boltzmann equation, $S_{conf} = k_B \ln \Omega$. On that basis, a recent discussion has drawn two inferences: (a) S_{conf} is lost when a liquid vitrifies and thus a glass has no residual entropy, S_{res}, and (b) structural relaxation of a glass would first increase its S_{conf} with time from its zero value and then decrease S_{conf} to the equilibrium value, thus causing the slope of its free energy against time plot to abruptly decrease after a certain time period. Both conclusions conflict with the classical, textbook analysis of the calorimetric data, and with the experimental findings. To evaluate the merits of these conclusions, we use the difference between the free energy of glass (and of supercooled liquid) and its crystal phase. If the inferences based on the statistical view are valid, (i) this difference would show a gap between the glass and supercooled liquid in the T_g range, (ii) the slope of the plot of this difference against T would be much less at $T < T_g$ than at $T > T_g$, and (iii) annealing would decrease this difference by a relatively large amount. After constructing such plots from the known C_p data, we propose that measurement of the vapor pressure, sublimation rate, solubility, chemical reaction rate, and emf of a cell made from glassy-metal electrodes may be useful for testing whether or not S_{conf} is lost on vitrification. The data available provide no support for the entropy-loss view.

1. Introduction

In undergraduate textbooks of physical chemistry and in monographs on glasses, non-crystalline solids are treated as structures with a kinetically frozen configurational entropy, S_{conf}, that persists on cooling to absolute zero temperature. It is therefore considered that such non-equilibrium solids have residual entropy, S_{res}, and therefore they violate the third law of thermodynamics. Classical thermodynamic relations derived for a reversible process are generally used to determine S_{res} of the non-equilibrium state from the calorimetric data, and S_{res} value is listed for a variety of materials. Its magnitude is interpreted to develop thermodynamics of the glassy state and in some cases the possibility of localized molecular motions in it.

According to statistical thermodynamics, $S_{conf} = k_B \ln \Omega$, where k_B is the Boltzmann constant and Ω the number of configurations of equal energy. Since the structure of a non-crystalline solid is fixed, Ω is equal to 1, and therefore its S_{conf} should be zero. In this view, a non-crystalline solid, like a perfect crystal, obeys the third law. It is not clear whether Ω refers to the number of configurations *available* to a structure or to the number of configurations *accessible* to the structure, though one accepts that not all configurations are explored in a realistic time. (There are $(3/2)^{6.03\times10^{23}}$ configurations of equal energy available to the structure of ice at 270 K. Even if the change from one configuration to another took only 1×10^{-12} s, it will take more than our life time for the ice structure to explore its all $(3/2)^{6.03\times10^{23}}$ configurations. Such an analysis is also the basis of the Levinthal paradox on biological function of proteins.) Despite that, undergraduate textbooks and monographs describe the S_{res} of non-equilibrium state of orientationally disordered crystals, such as ice and solid CO, as determined by classical thermodynamic relations and calorimetric data. These analyses show that the S_{res} agrees with the S_{conf} obtained from the Boltzmann equation with Ω equal to the number of configurations *available* to a structure.

During the 20th century, every new generation brought forth the above-mentioned conflict between the statistical and calorimetric entropy views and discussed it, time and again, in terms of the Clausius ansatz, the Boltzmann equation and the "Maxwell's demon", and thereafter continued to use the classical thermodynamic view, without looking into the possibility of experimentally verifying either of the two views. Its history has been given briefly in several papers [1–5]. The discussion was re-opened in 1999 [1], with focus on the possible loss of S_{conf} when a liquid vitrifies on cooling. In the statistical entropy view, a glass should have no S_{conf} because there are no structural fluctuations within the same energy and volume of a glass and, therefore, most of S_{conf} should vanish when a

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liquid vitrifies. In the classical thermodynamic view, S_{conf} of a liquid becomes kinetically frozen when it vitrifies on cooling. We refer to these mutually exclusive views as the "entropy-loss view", and the "classical view". Goldstein [3] critically discussed the arguments given for the entropy-loss view and found that the arguments are untenable. He concluded that a liquid does not lose entropy on vitrification and therefore a glass has finite S_{res}, as described in the textbooks. Gutzow and Schmelzer [4] investigated the merits of the entropy-loss view, discussed the evolution of the third law and theoretical aspects of the entropy of a non-equilibrium state, and described several careful experiments on the solubility and other properties of glasses that had been overlooked in Refs. [1,2,5]. They too demonstrated the existence of frozen-in S_{conf} of glasses and its dependence on vitrification kinetics, thus concluding against the validity of the entropy-loss view. In response, Reiss [5] appealed that a finite value of S_{res} violates the causality principle. Reiss went on to suggest that the impression of S_{res} stems from inclusion of a *path-irreversible* segment in the thermodynamic cycle of the liquid and glass, and the value of S_{res} is an artifact from use of the specific heat, C_p data, in this segment [5]. (This issue was discussed at two workshops: (1) *Glass and Entropy, International Workshop on Glass and Entropy*, Trencin, Slovak Republic, 25–27 June 2008 and (2) *Glass and Entropy II*, Aberystwyth, U.K., 22–24 April 2009.)

Those who use classical thermodynamics admit that, strictly speaking, the $C_p \, d\ln T$ integral should not be used to estimate entropy in a temperature range where C_p changes with time or where the C_p measured during cooling differs from that measured during heating at the same rate. Goldstein [3] showed that the effect of time-dependent C_p is very small, and inconsequential for the classical calorimetric analysis for S_{res}. In an alternative suggestion, the observation time has been considered as an auxiliary constraint in the loss of S_{conf} [1–5] on vitrification of a liquid. The enthalpy H and the volume V do not change on vitrification and are not subject to this constraint.

To summarize, in the entropy-loss view, S_{conf} vanishes when a liquid vitrifies and S_{res} of a glass is zero, like that of a perfect crystal. The question one may ask is: where does the entropy go when a liquid vitrifies and the structure does not change? On structural relaxation during annealing, S_{conf} of a glass would therefore first increase from zero and then decrease to its equilibrium (or ultimate) value. In the classical view, S_{conf} becomes kinetically frozen when a liquid vitrifies and S_{res} of a glass is finite, and during structural relaxation during annealing, S_{conf} would monotonically decrease to the equilibrium value. The two views are mutually exclusive. Although it is necessary that experiments be suggested to evaluate these views, those who propose the entropy-loss view have suggested no experiment to do so. Vapor pressure and solubility measurements are useful for evaluating the two views, but the validity of their relation with the free energy of a non-equilibrium state rests on certain assumptions. Goldstein [3] discussed the ratio of the solubility of a glass to that of its crystal state, and analysed the source of difficulties in measuring this ratio. However, the solubility ratio has been found to depend upon the solvent and on ionic or other equilibrium in the solution. Here we avoid theoretical approaches and the terminology used by others [1,2,5]. Instead, we use the known relations between the properties of an *equilibrium* state of a material with its free energy and propose experiments for resolving this issue. In regard to the use of such relations for a glass, we begin by pointing out that even crystalline solids, whose S_{res} is taken to be zero, contain kinetically frozen point defects, impurity atoms and dislocations and, therefore, like glasses, are also in a non-equilibrium state. Strictly speaking, their S_{res} is not zero. We also argue that formation of amorphous germanium by electrolysis of $GeCl_4$ solution is indication that the free energy relations may be valid for non-equilibrium solids.

2. The entropy and free energies in the entropy-loss and classical views

Certain experimental features of glass formation and glass have been accepted since the 1920s and these are common to both the entropy-loss and classical views, as follows: there is no loss of H and V on cooling through the vitrification temperature range. The elbow-shaped plots of their H and V against T show a time-dependent decrease in the slope [6–9] in the vitrification range. Vitrification occurs at a higher T when the cooling rate is high and at a lower T when it is low. Structural relaxation that occurs on annealing of glass decreases its H and V with time until the equilibrium values are reached. These features characterize the glass-softening or glass-transition temperature T_g as well as its fictive temperature T_f. Excess entropy S_{exc} of liquid and of glass over the crystal state is calculated from their respective excess specific heats by using the integral of $C_{p,exc} \, d\ln T$, from the melting point T_m to $T \to 0\,K$. Since the properties of a glass depend upon time used to measure it, the properties are not a function of state in the same sense as they are assumed for (ordered but defect-containing) crystals, unless provision could be made to include time as a variable.

For clarity, we henceforth use the term σ_{exc} for the excess entropy and the term Γ_{exc} for the free energy of the glass in the entropy-loss view, and S_{exc} and G_{exc} for the corresponding properties in the classical view. In the entropy-loss view [1,2,5], the S_{conf} part of the entropy is lost on cooling through T_g. This loss is seen to be equal to S_{res} when contributions from molecular motions in the glassy state are ignored [1,5]. Thus, at $T < T_g$, σ_{exc} is considered to be entirely due to excess vibrational contributions [1,5]. In that case a glass would have only a vibrational contribution at T just below T_g, regardless of how it was produced, whatever rate the liquid was cooled to produce it, and howsoever the glass was annealed.

It is known [10] that H and S of a glass have contributions from the availability of configurations from two other kinetics, the faster modes of motions in the distribution of times of the α-relaxation process, and localized molecular motions known as the β- or JG-relaxation. Gupta and Mauro [2] took into account only the contribution from β- or JG-relaxation relaxation in simulating the structural relaxation of a glass. In a real case, σ_{exc} contains the above-mentioned two relaxational contributions which, along with the excess vibrational contributions, would vanish on cooling to 0 K. Because of the relaxational contribution, σ_{exc} of a glass also would be time-dependent in the temperature range of kinetic-freezing of the underlying molecular motions. Although, the effect is small it does raise the same problem of determining the entropy of the non-equilibrium state as of determining it in the glass transition region.

In the classical thermodynamics view, there is no loss of entropy when a liquid vitrifies on cooling. Just like the plot of H and V, the plot of S against T also has an elbow-shape and a time-dependent decrease in the slope [6–9] in the vitrification range. It too characterizes its T_g. The configurational part of the entropy becomes kinetically frozen-in on cooling through T_g and persists at 0 K, and thus a glass has a finite S_{res}. Its value is higher the higher is the rate of cooling of a glass. Its magnitude decreases when the glass structurally relaxes during annealing.

More important to our discussion is the excess free energy, $\Gamma_{exc} = H_{exc} - T\sigma_{exc}$ and $G_{exc} = H_{exc} - TS_{exc}$. In the entropy-loss view, Γ_{exc} abruptly increases as most of the S_{conf} part of the entropy vanishes on cooling through the T_g range. Since T_g depends upon the rate of cooling a liquid, the abrupt loss of the free energy on vitrification would not be seen as the zeroeth order transitions in Ehrenfest's classification. Despite that, those who support the entropy-loss view assert that the increase in the free energy at T_g is equal to T_gS_{res}. In the classical view, G_{exc} does not change and its plot against T shows only a time-dependent increase of slope on cooling through T_g [6–9], as dS_{exc}/dT decreases at T_g. The slope of G_{exc} against T decreases slightly as a glass is cooled to 0 K.

The entropy and free energy of a glass are usually determined by assuming that C_p has been measured for an equilibrium state and vitrification is a reversible process, i.e., input of heat becomes the output of heat to yield the same value of C_p on heating and cooling. Goldstein [3] has argued that the process is reversible if the cooling and heating rates were the same and structural relaxation could be avoided. (To recall, the majority of crystals are not in a thermodynamic equilibrium state because they contain kinetically frozen point defects. At high temperature they have a configurational entropy, like liquids, but as a result of different arrangements of these defects in the crystal lattice.) We should also note that temperature modulated calorimetry for low modulation frequencies and slow cooling and heating rates yields the same C_p values on heating and cooling through the T_g range. But it does not do so over the entire temperature range extending to 0 K. Rather the region in which C_p values on cooling and heating may differ becomes shifted to lower temperatures and the difference is reduced. Decreasing the modulation frequency and the cooling and heating rates accordingly further decreases this difference. Since a lower modulation frequency yields the same C_p on cooling and heating, this technique would yield a value of S_{conf} that more closely justifies the use of classical thermodynamic relations than adiabatic calorimetry. On the opposite end, fast calorimetry can yield the vibrational part of the entropy more accurately and at higher temperatures than adiabatic calorimetry.

For instructive purposes, one may construct a figure containing two plots of the excess entropy against T, one from 0 K to T near T_g by using the $C_{p,exc}\,d\ln T$ integral, and the second from T_m to T_g by subtracting the $C_{p,exc}\,d\ln T$ integral from the entropy of fusion. The integral from 0 K to T_g would be for the non-equilibrium state of a glass, but as long as its C_p can be reversibly measured in an experiment, i.e., in the absence of structural relaxation of glass, the integral would yield the excess entropy. The two plots would show a gap at T near T_g. This gap would be equal to the S_{conf} lost on cooling through T_g in the entropy-loss view, and it would be equal to S_{res} in the classical view. Increase in the cooling rate would shift this gap to a higher T and make it bigger, and decrease in the cooling rate would shift it to lower T and make it smaller. In the method used in textbooks the $C_{p,exc}\,d\ln T$ integral taken from the liquid at T_m to glass at 0 K and subtracted from the entropy of fusion. The subtraction does not consume all the entropy of melting and whatever is left at 0 K is called the residual entropy, S_{res}. In this construction, the plot of S_{exc} against T is continuous and shows an elbow-shaped change in slope in the T_g range.

When a glass is formed by rapid cooling or hyperquenching of a liquid, or when a non-crystalline solid is produced by vapor deposition, chemical reaction, lyophilization, mechanical deformation of a crystal, collapse of a crystal under pressure, or high-energy irradiation of a crystal, S_{res} of the state formed is higher than that of the glass formed by normal supercooling of a liquid. Like those of normal glasses, their H and S also decrease on cooling toward 0 K as contributions from molecular vibrations, from the faster modes in the distribution of times of the α-relaxation process, and from localized molecular motions decrease. As a consequence, H and S of such glasses would decrease more than that expected from the phonon contribution alone, and Γ_{exc} and G_{exc} would *increase* more rapidly toward H_{exc} at 0 K.

3. Quantitative features of the entropy and free energy in the two views

For quantitative discussion, we use Hikima et al.'s [11] data for C_p of triphenylethene in its glass, liquid and crystal states. Its melting point, T_m, is 341 K, the enthalpy of fusion is 20.35 kJ/mol, T_g as determined by adiabatic calorimetry is 248 K and S_{res} of the glass obtained by cooling the liquid at 10 K/min is 18.6 J/(mol K) [11]. Its H_{exc} is plotted against T as curve 1 in Fig. 1(a), which includes two plots for the equilibrium state, one obtained by interpolation of $C_{p,exc}$ [12], such that $S_{exc} \to 0$ as $T \to 0$ K, and the second obtained for H_{exc} in the Kauzmann extrapolation such that $S_{exc} \to 0$ at T_k, which is 202.6 K (see Ref. [12] for details). At $T < T_k$, the magnitude of H_{exc} remains constant on cooling to 0 K. The plots of S_{exc} against T calculated from the $C_p\,d\ln T$ integral are shown in Fig. 1(b). The $C_{p,exc}\,d\ln T$ integral from 0 K to T_g yields the same value for σ_{exc} and S_{exc}. At T_g of 248 K, the gap of 18.6 J/(mol K) between σ_{exc} and S_{exc} of the supercooled liquid is equal to the S_{conf} lost in the entropy-loss view, and it is equal to S_{res} in the classical view. Fig. 1(b) also includes two plots for the perceived equilibrium state at $T < T_g$, one for $S_{exc} \to 0$ at T_k of 202.6 K in the Kauzmann extrapolation [12] and the other for $S_{exc} \to 0$ as $T \to 0$ K in the C_p interpolation [12].

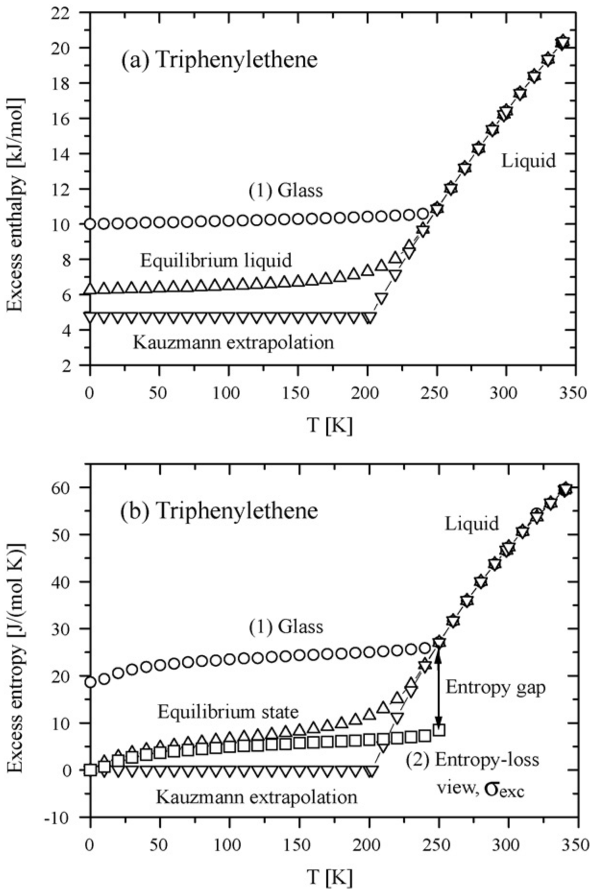

Fig. 1. (a) Plots of the excess enthalpy of liquid and glassy states of triphenylethene with temperature. The excess enthalpy does not change on vitrification at 248 K. (b) The corresponding plots of the excess entropy. Notation σ_{exc} is used for the entropy-loss view, in which the gap between the excess entropy of a glass and that of a supercooled liquid at T_g is equal to S_{conf} lost on vitrification. In the classical view, the same gap is equal to the residual entropy. Also shown is the variation of the excess enthalpy and entropy of the supercooled (equilibrium) liquid in both the Kauzmann extrapolation and the C_p interpolation. The C_p data used in the analysis are taken from Hikima et al. [11] and analysed earlier in Ref. [12].

Since we will compare the entropy-loss view against the classical view, we have included curve 1 for S_{exc} in Fig. 1(b). This is obtained either by adding S_{res} to the curve labeled σ_{res} or by subtracting the $C_{p,exc}\,d\ln T$ integral from the entropy of fusion beginning at T_m, as described above and in the literature [6–9]. In the entropy-loss view, S_{exc} abruptly decreases from 26.8 J/(mol K) to σ_{exc} of 8.2 J/(mol K), and in the classical view (curve 1), it does not change

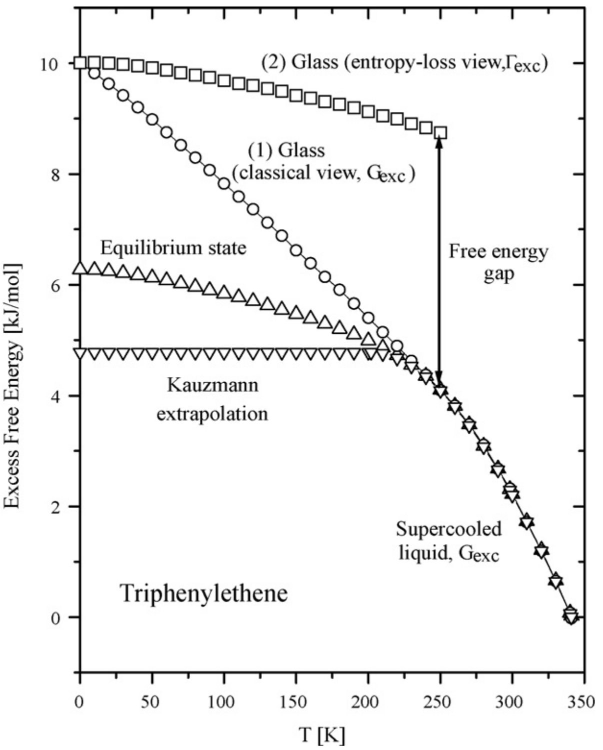

Fig. 2. Plots of the excess free energy of liquid and glassy states of triphenylethene with temperature. Notation $\Gamma_{exc} = H_{exc} - T\sigma_{exc}$ is used for the entropy-loss view in which there is a gap between the excess free energy of a glass and that of a supercooled liquid at T_g. In the classical view there is no such gap. The magnitude of this gap is equal to $T_g(S_{conf})$ at T_g. Also shown is the variation of G_{exc} in both the Kauzmann extrapolation and the C_p interpolation. The C_p data used in the analysis are taken from Hikima et al. [11] and analysed earlier in Ref. [12].

at T_g. Both S_{exc} and σ_{exc} thereafter decrease slowly to zero at 0 K, as the excess contributions from molecular vibrations, from faster modes of the distribution of relaxation times of the α-relaxation process, and from those of the localized relaxations described above decrease to zero. A supercooled liquid in internal equilibrium would also lose its S_{exc} on cooling in two ways, as shown in Fig. 1(b). It may decrease either progressively more rapidly to zero at T_k, as in the Kauzmann extrapolation or decrease slowly to zero at 0 K along a sigmoid shape path as in the C_p interpolation [12].

The excess free energy of triphenylethene was calculated from the data in Fig. 1(a) and (b) [12] and it is plotted against T in Fig. 2. In the entropy-loss view, its value abruptly increases on cooling through T_g by 4.61 kJ/mol to its Γ_{exc} value in curve 2, and thereafter Γ_{exc} increases slowly to 10.02 kJ/mol as $T \to 0$ K. In the classical view, the plot is continuous and its slope slightly increases on cooling through T_g and remains higher for the glass than for the liquid until $T \to 0$ K where G_{exc} reaches 10.02 J/mol. The slope of the G_{exc} plot is more than that of the Γ_{exc} plot. Also shown are the plots of the internally equilibrated state in the Kauzmann extrapolation, in which G_{exc} becomes constant at 4.76 kJ/mol, as well as in the C_p interpolation in which G_{exc} increases progressively more slowly to 6.25 kJ/mol at 0 K. If the vibrational entropies of the crystal and glass were the same and the liquid was to lose all its S_{conf} on vitrification, its σ_{exc} and Γ_{exc} would be zero. Its free energy at $T < T_g$ would be the same as that of the crystal.

4. Experiments for testing the entropy-loss view

In fairness to the arguments of Kivelson and Reiss [1], we may begin by *assuming* that the entropy-loss view has merit, and determine what consequences it has that can be tested by experiments. This is important because they suggested no laboratory experiment to test the validity of their view. If experiments do not support these consequences, the entropy-loss view may not be worth maintaining. Gupta and Mauro [2] attempted to strengthen the Kivelson and Reiss [1] view by computation of an approximate model for a liquid and glass in the enthalpy landscape paradigm. They used the term ergodicity-breaking in their view of laboratory glass formation instead of the usually considered structural arrest by a kinetic freezing, and simulated in a special case the change in S and G with time when a glass structure relaxes on isothermal annealing [2]. Their model was flexible enough to produce different manners of increase in the entropy from zero to the equilibrium value.

Kivelson and Reiss [1] and Reiss [5] argued that the irreversible segment of the thermodynamic path of C_p between a liquid and glass is to be avoided for determining the entropy change. But as mentioned earlier here there is more than one irreversible segment of this thermodynamic path if one extends the path from liquid to 0 K. One segment is of course in the T_g range, and is relatively sharp. Other segments are more gradual and they are in their own characteristic temperature range between 0 K and T_g. As was implicit in Goldstein's analysis, one can avoid the entropy determination from the $C_p\,\mathrm{d}\ln T$ integral and discuss the issue of S_{res} in terms of the free energy. Here we similarly circumvent the entropy issue and consider how the change in free energy determined by independent experiments would appear in the entropy-loss view. We distinguish this free energy change by the term ΔG_{exc}. If ΔG_{exc} is found to be qualitatively consistent with Γ_{exc}, the entropy-loss view would be valid. Alternatively, one may subtract ΔG_{exc} from H_{exc} and determine the excess entropy, $\Delta S_{exc} = (H_{exc} - \Delta G_{exc})/T$. If ΔS_{exc} is found to be consistent with σ_{exc} then the entropy-loss view would be valid.

The quantity ΔG_{exc} may be determined from measurements of the vapor pressure, sublimation rate, solubility, chemical reactivity of both the glass and its crystal state, and from emf of a cell with one electrode constructed from the glassy state and the other from the crystalline state or any other configuration, as elaborated below.

(i) The vapor pressure, $p_{vap} \propto \exp(G/RT)$. In the entropy-loss view, the configurational part of the entropy is lost on cooling through T_g, and therefore Γ would abruptly increase. This means that p_{vap} would decrease by a factor of $\exp(S_{conf}/R)$ when a liquid vitrifies. The reverse would occur on heating a glass through T_g and p_{vap} would abruptly decrease. There would be no such change in the classical view. For a quantitative test, one may determine Γ_{exc} and G_{exc} from the $C_{p,exc}$ data. On cooling a liquid G_{exc} would decrease to Γ_{exc} at T_g by an amount T_gS_{conf}, which is the same as T_gS_{res}, and on heating the glass Γ_{exc} would increase to G_{exc} by about the same amount. For triphenylethene, S_{res} is 18.6 J/(K mol) and T_g is 248 K [11], and on cooling its G_{exc} increases by ~4.61 kJ/mol to Γ_{exc} in curve 2. Its p_{vap} would increase abruptly by an amount corresponding to ~4.61 kJ/mol on cooling through 248 K. (For glasses of higher T_g and/or higher S_{res}, the increase in G_{exc} would be higher, and therefore the increase in p_{vap} would be higher. For example, tri-α-naphthylbenzene, whose S_{res} is 33 J/(K mol) and T_g is 342 K [10], would show an increase in G_{exc} of 11.29 kJ/mol and correspondingly large increase in p_{vap} on cooling its liquid through 342 K.) Since a faster rate of cooling produces a glass of higher S_{res} at a higher temperature, the change in G_{exc} to Γ_{exc} and in p_{vap} would be higher at that temperature.

On the basis of the features of the plots shown in Fig. 2, the entropy-loss view has at least four experimentally testable consequences for p_{vap}: (a) the measured p_{vap} would show a discontinuity in the T_g range. (b) The change in p_{vap} at the discontinuity would correspond to the change in G_{exc} which is equal to T_gS_{res}, and therefore the measured change in p_{vap} would yield a reasonable value for the S_{conf} lost, or of S_{res}. (c) Variation of p_{vap} with T would be smaller at $T < T_g$ than at $T > T_g$ and it would correspond to the slopes

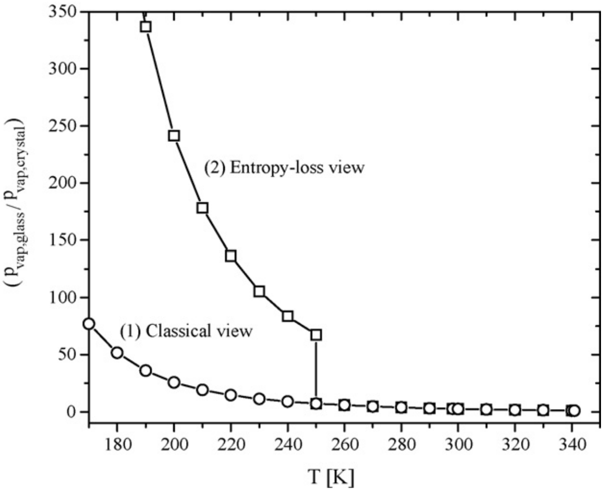

Fig. 3. Plots of the vapor pressure ratio of the glassy to crystalline states of triphenylethene calculated from the data plotted in Fig. 2. The corresponding ratios for the sublimation rate and for the solubility would be similar. A crucial test for the entropy-loss view would be to determine if the ratio abruptly increases on cooling through the T_g of a material.

of their G_{exc} plots, and (d) on annealing a glass at T just below T_g, the decrease in p_{vap} would be relatively high value, *close* to the magnitude corresponding to $T_g S_{res}$.

(ii) For a one-component system, the ratio of p_{vap} of glass to p_{vap} of the crystal phase is given by

$$\left(\frac{p_{vap,glass}}{p_{vap,crystal}}\right)_T = \exp\left(\frac{\Delta G_{exc}}{RT}\right) \qquad (1)$$

If ΔG_{exc} determined from p_{vap} measurements is found to be equal to Γ_{exc}, or else Γ_{exc} yields the same p_{vap} ratio as measured, the entropy-loss view would be valid. To illustrate, we calculated the p_{vap} ratio for triphenylethene from the Γ_{exc} and G_{exc} data in Fig. 2, and have plotted it against T in Fig. 3. The plot is limited to $T > 130$ K. Curve 2, which is for the entropy-loss view, i.e., calculated from Γ_{exc}, shows an abrupt change at T_g. But curve 1, which is for the classical view, i.e., obtained from G_{exc}, shows a continuous change in the T_g range.

To determine ΔG_{exc} from the p_{vap} ratio, one may perform two experiments at the same T, in one $p_{vap,\,glass}$ may be measured, and in the second $p_{vap,\,crystal}$ be measured. Alternatively, one may perform only one experiment in which p_{vap} of the same sample is measured before and after crystallization of its glassy state and compare the ΔG_{exc} obtained against Γ_{exc} and G_{exc}. At 230 K in Fig. 2, $\Gamma_{exc} = 8905$ J/mol and the p_{vap} ratio is 105.4, and $G_{exc} = 4628$ J/mol and the p_{vap} ratio is 11.2. If p_{vap} measurements for triphenylethene glass and crystal were to yield a ratio close to 100, the entropy-loss view would be valid, otherwise it would not. For a further quantitative test, one may measure the p_{vap} ratio as a function of T and compare the slope of the p_{vap} ratio against T plots with the slopes of the Γ_{exc} and G_{exc} against T plots in Fig. 2. If the slope agrees with the slope of Γ_{exc} plot, the entropy-loss view would be validated.

In general, G_{exc} of a (non-equilibrium) glass is higher than G_{exc} of its equilibrium state at the same T, irrespective of one's choice for determining it by using the Kauzmann extrapolation or C_p interpolation [12]. Also, the excess free energy of glass decreases on structural relaxation during annealing at a fixed T. (It would decrease to zero also but abruptly if the glass crystallizes.) If a glass is annealed at T just below T_g, the decrease in $p_{vap,\,glass}$ to the equilibrium value in the entropy-loss view would be many times larger than in the classical view. The decrease in Γ_{exc} estimated from the data in Fig. 2 is by 4630 J/mol at 240 K, and that estimated from G_{exc} is only by 91 J/mol. We also suggest that if the absolute p_{vap} value cannot be determined, one may measure the ratio of $p_{vap,\,glass}$ to p_{vap} of the equilibrium state after structurally relaxing the glass. If the ratio were found to be close to 10 for triphenylethene, the entropy-loss view would be valid.

(iii) The sublimation rate of a glass and crystal has the same relation with the free energy as p_{vap} and its ratio is the same as the ratio of p_{vap} in Eq. (1) for the condition that molecular sticking coefficient is equal to 1, as assumed by Speedy et al. [13] for amorphous solid water obtained by vapor deposition on a substrate. Therefore, the sublimation rate would show all the features described above in (i) and (ii), and one may use this ratio in place of the p_{vap} ratio to test the validity of the entropy-loss view.

(iv) The ratio of the solubility of a glass and its crystal form is also given by Eq. (1), and Goldstein [3] has already considered this ratio. It may also be used instead of p_{vap} and it would show all the above-described features in (i) and (ii), as long as there is no significant interaction between the solute and solvent molecules.

(v) When a material chemically reacts with gases or with another substance in a mixture, the activation energy for the reaction is determined by the difference between the free energy and the activation barrier height. If the free energy of a material is already high, its value would be closer to the top of the barrier and the activation energy, E_a, for the chemical reaction would be lower. Therefore, the rate of the chemical reaction of a given material would vary according to the difference between its own free energy and the barrier height. (This is apparent, for example, as accelerated corrosion of iron structures in the areas of high-strain, where its free energy is higher.) Therefore, the high Γ_{exc} and G_{exc} of a glass and other non-crystalline solids would lower its E_a for chemical reaction with gases, solids and other states. This means that if the rate of chemical reaction of a liquid state of a material is measured as a function of temperature, it would change continuously on cooling by an amount that is higher than the value expected from the change in T alone. The change in the reaction rate would be in a direction opposite to that observed in p_{vap}, the sublimation rate or the solubility ratio.

Since Γ_{exc} is much higher than G_{exc} of the supercooled liquid, E_a would show an abrupt decrease on vitrification of a liquid at T near T_g in the entropy-loss view, and thereafter E_a for the glassy state would decrease slowly with decrease in T. In contrast, in the classical view, there would be no abrupt decrease E_a since G_{exc} changes continuously through T_g and E_a for the glassy state would decrease more rapidly on cooling. The above-given experiments (i) and (ii), but designed to measure the chemical reaction rate can also be used to determine the change in E_a. Moreover, as both Γ_{exc} and G_{exc} decrease by structural relaxation on annealing and the glass approaches its equilibrium state, E_a would increase and the reaction rate would decrease with time. The amount of decrease would be much larger in the entropy-loss view than in the classical view. The change in the reaction rate here also would be in a direction opposite to that observed in p_{vap}, rate of sublimation or solubility.

(vi) The emf of an electrolytic cell is given by $E^0 = -\Delta G^0/zF$, where ΔG^0 is the free energy change for the chemical reaction, z is the number of electrons that exchange between a metal electrode M, and its ions M^+ in a solution involving a chemical equilibrium, $M^{z+} + ze^- = M$, F is the Faraday constant and e^- refers to the electron. The emf is estimated by considering the chemical potential of the two electrode materials, of the respective ions of each material in a solution and of the electrons. Now, any change in G of an electrode's metal would contribute to ΔG^0, and this would be observed as a change in E^0 of such a cell, assuming that the chemical potential of electrons in the metal remains unchanged. Therefore, one may construct a Daniel cell containing one electrode made of a glassy metal, M_{glass}, immersed in a solution containing M^+ ions and the second electrode made of a different (crystalline) metal, M_1, in a solution containing M_1^+ ions. (The chemical reactions are: $M_{glass} = M^{z+} + ze^-$ and $M_1^{z+} + ze^- = M_1$.) The free energy of the net chemical reaction calculated from the emf of this cell should be equal to the value calculated from the free energies of M_{glass} and M_1 either in the classical view or in the entropy-loss view, but one would not be able to discern which view. To discern it, one may construct another Daniel cell in which the electrodes of both metals are crystalline and the reactions are: $M = M^{z+} + ze^-$, and $M_1^{z+} + ze^- = M_1$. If both cells are heated through a range that includes the T_g range of M_{glass}, the free energy of M_{glass} in the entropy-loss view would decrease from Γ_{exc} to G_{exc} and this would decrease the difference between the emf of the two cells. The decrease may be equal to either that expected from the entropy-loss view or to that expected from the classical view. Alternatively, on cooling through the vitrification range, the difference would increase but in a different range of T than that of its decrease. It would also correspond to only one of the two views. Obviously, several such combinations of electrodes may be used in a Daniel cell.

One may also use a cell in which electrodes of the same metal M are immersed in the same solution of M^+, but one electrode is in the glassy state and the other in the crystalline state. Its emf would be consistent with either Γ_{exc} or G_{exc}. Also, a cell with both electrodes made from a glassy metal, but one in a highly non-equilibrium state and another in its equilibrium disordered state may be used. Its emf also would be consistent with only one of the two views. As the free energy of M_{glass} decreases with time, the emf of the cell containing a glassy-metal electrode would change with time, according to the free energy decrease in only one view. As an illustration, if Γ_{exc} ($=T_gS_{res}$) of the metal used as an electrode increased by 4.61 kJ/mol on cooling through 248 K, as in Fig. 2, the increase in emf for $z = 2$, would be by 23.9 mV in the entropy-loss view, and none in the classical view. Moreover, since T_g of metals is high and S_{res} substantial, the actual emf observed in an experiment would be higher than the value given.

5. Discussion

Data on vapor pressure, sublimation rate, solubility ratio, chemical reaction rates, and emf for the glassy and non-crystalline materials are scarce. We found p_{vap} data only for one single-component material, the element argon in a paper by Kouchi and Kuroda [14]. They made amorphous solid films of Ar by vapor deposition at 10 K and reported its p_{vap} at T from 14 K to 27 K. On heating the film at 2 K/min they found that amorphous Ar began to transform to fcc Ar at 20 ± 1 K and the transformation ended at 24 ± 1 K. They also measured p_{vap} of the crystal from 25 K to 28 K. (For more description, see Fig. 3.16 in Ref. [8].) They reported that the ratio of p_{vap} of the amorphous to crystalline phase is ~100 [14]. Estimate of this ratio at 20 K, which requires the least extrapolation of the p_{vap} of fcc Ar, yields G_{exc} of ~766 J/mol. This needs to be compared against Γ_{exc} and G_{exc}, but $C_{p,exc}$ data needed to determine these quantities are not available. Nevertheless, the data show no decrease in p_{vap} of the glass at T_g before crystallization began on heating. These results seem to provide no support for the entropy-loss view.

The data on the sublimation (evaporation) rate of vapor-deposited water at 150 K [13] are for a state at $T > T_g$, and we do not use it for analysis.

Solubility measurements of the glass and crystal state of different materials are available in the literature. Data on the solubility of vitreous silica ($T_g = 1473$ K) and quartz in water have been compiled from various sources in Fig. 3.18 in Ref. [8]. These give a solubility ratio of ~2.8 at T of 513 K. Like the calculated p_{vap} ratio in Fig. 3 here, the solubility ratio would decrease abruptly on heating through its T_g of 1473 K, and therefore this ratio for silica glass would be much less than 2.8 at T_g. The ΔG_{exc} obtained from it would not be high enough to support the entropy-loss view. Data on the solubility of crystalline and glassy Se ($T_g = 303$ K) in CS_2 and of crystalline and glassy As_2O_3 ($T_g = 430$ K [15]) in water have also been plotted against T by Gutzow and Schmelzer in Fig. 3.18 in Ref. [8]. For Se, the plots give a solubility ratio of only 1.8 at T_g of 303 K and there was no evidence for an abrupt increase in this ratio on cooling through T_g. For As_2O_3, their plots give a solubility ratio of 1.6 at 357 K and it would be much less at T_g of 430 K mentioned above. This also does not indicate a sufficiently large change in the ratio to support the entropy-loss view. Grantcharova and Gutzow [16] have also provided accurate data on the solubility of crystalline and glassy states of phenolphthalein ($T_g = 353$ K) in water. From Fig. 3.20 in Ref. [16] we find the solubility ratio of ~7 at 295 K and ~4 at T_g. The solubility ratio of 4 at T_g yields an S_{res} of ~5 J/(mol K) when contributions to entropy from molecular motions in the glassy state are neglected, but there seems to be no indication of an abrupt increase in this ratio at T near T_g.

Numerous data are available on the solubility ratio of pharmaceuticals [17]. These data have been compared against the value predicted from their G_{exc}, i.e., in the classical view. The expectation was that C_p data could be useful in predicting the solubility ratio via the calculation of G_{exc}. In some cases, the ratio agreed with the value predicted from G_{exc} and in others it did not [17]. Those for which it did not, the predicted value of the solubility ratio was higher than that measured. (Note that Γ_{exc} is higher than G_{exc}, and therefore it would have made the predicted value even more higher than the measured values.) As mentioned before, interactions with the solvent molecules and the ionic equilibrium in it, as well as history of a glass have an effect on both the measured and predicted solubility ratios. Though it is not certain why the measured and the predicted ratios from G_{exc} differ, the agreement found for some pharmaceuticals indicates that classical view is useful.

Although Eq. (1) applies only to a one-component system, some of the findings for other systems are worth noting. Überreiter and Bruns [18] measured p_{vap} of a solution of polyvinylcarbosolon in benzene. Their plots of $\log_{10} P$ against $1/T$ for the glass and liquid, where P is the ratio of p_{vap} of solution to p_{vap} of the solvent, appear also in Fig. 3.17, Ref. [8]. At T_g of 298 K, the plot gives $\log_{10} P$ as 1.45. At 302 K, the $\log_{10} P$ value is 1.4 for the glass and 1.3 for the equilibrium state, thus showing that P decreases on stabilization (annealing) of the glassy state of the solution. The decrease in P is by 21% (a factor of 0.79) and there is no indication of an abrupt rise in P on cooling the solution through its T_g of ~302 K.

Barcea and Wolfe [19] have reported p_{vap} data on solutions of poly(styrene) in cyclohexane of different volume fractions, φ. For a solution of $\varphi = 0.85$, T_g read from their Fig. 1 is 315 K [19]. They plotted a quantity p/p_0, i.e., p_{vap} of the solution normalized by that of cyclohexane, in their Fig. 3 [19]. From it, the p/p_0 values read are: 0.663 (305 K), 0.658 (307 K), 0.646 (309 K), 0.596 (313 K) and 0.584 (333 K). On cooling, p_{vap} of both the solution and cyclohexane decrease. Vapor pressure of cyclohexane, p_0 is higher than that of solution and it changes more with changing T. Therefore, the quantity p/p_0 would decrease on cooling to a lesser extent than p_{vap} of the solution would decrease. Even with such a decrease included in p/p_0, there is no indication for an abrupt rise in p_{vap} of the solution on cooling through its T_g of 315 K.

The p_{vap} ratio of tellurium for the $Ge_{14}Te_{84}$ alloy has been estimated by Bergman and Chastel [20] from measurements of the ion intensity, I_{Te}, by using the Knudsen cell mass spectrometry. The glassy state of their alloy was obtained by quenching the melt at 873 K in salt water and measurements were made during heating of the quenched sample. The quantity $\log_e(I_{Te}T)$ was found to increase toward a plateau-like value at $T < 400$ K, in a manner similar to that observed for amorphous Ar in Fig. 2 of Ref. [14], and thereafter it increased toward a value for a state that was found to be crystalline on the basis of the data obtained by thermal cycling of the sample.

They did not determine T_g of the $Ge_{14}Te_{84}$ alloy by calorimetry, and gave its value as 410 K based on the ionic intensity data. (T_g marked in their Fig. 3 is less than 400 K [20].) The purpose in their study was to determine whether or not a metallic glass has a higher p_{vap} than its crystal phase, and they concluded that the p_{vap} ratio is 100. This corresponds to ΔG_{exc} of 6817 J/mol at T_g, but as its $C_{p,exc}$ data are not available, we cannot compare it against G_{exc} or Γ_{exc}. Since the amount of crystallization on heating through T_g is also not known we do not extrapolate the $\log_e(I_{Te}T)$ value from high temperature to obtain p_{vap} of the equilibrium state at $T < T_g$ in order to use criteria (d) given in Section 4. Nevertheless it is clear from the plot in their Fig. 4 [20], that there is no abrupt decrease in p_{vap} of the glass on heating through T_g. Instead, the continuity of the plot would seem to be consistent with the classical view.

6. The free energy and its relation with other properties

The relation of free energy with the various properties of glass, which we have used here and others have used before, may be questionable. The reason is that such a state may not be in reversible equilibrium with its vapor. This aspect has been discussed variously in the literature [3,8,13,14], where references dating back to 1920s may be found. To elaborate, a layer of deposited vapors on the surface of a glass (or on the surface of other non-crystalline solids) may not have the same structure and properties as the bulk state. Nevertheless, whatever structure and properties the (disordered and immobile) layer of deposited vapor on the surface of a glass may have, its S_{exc} would still be zero in the entropy-loss view, but its enthalpy may be different from that of the bulk state. Therefore, it would have the same qualitative consequence for Γ_{exc}, G_{exc} and related properties as would any other disordered solid state. It should also be noted that surface tension and impurity segregation on the surface of a crystal also cause their surface to have different structures and properties than the bulk. We point out that in the semiconductor technology, relation between p_{vap} and the free energy of equilibrium state is used for crystals in a non-equilibrium state, containing kinetically frozen point defects in greater population than in the equilibrium state [21]. To the extent that thermodynamic relations for such crystals are useful in that technology, these thermodynamic relations would be useful here.

We recall that classical thermodynamics mainly provides a formalism for macroscopic changes and, based on that, it makes predictions. The change may result from molecular relaxations and vibrations, from chemical reactions and phase transformations, but classical thermodynamics alone does not distinguish between such mechanisms. The discussion here, therefore, should not be used to indicate any particular mechanism, transient or otherwise for the changes in the entropy and free energy. Vapor pressure and sublimation (evaporation) rate of a solid (liquid) are described in terms of the bulk property, as they are done at the melting point of a crystal, and not in terms of the surface property although surface strains may have a small effect. Also, thermodynamics of solid–solid, solid–liquid and solid–gas reactions have been widely studied without reference to the mechanism of the reaction. As mentioned earlier here, increase in the free energy by any procedure would increase the reaction rate. One may recall commonly noted rapid corrosion in the elastically strained and in permanently deformed regions of iron metal structures where the bends are made or bolts have been tightened. Despite the above arguments, there are limitations in the use of the above-described procedures, and these limitations are yet to be investigated.

Reversibility of an electrochemical reaction between an amorphous solid and its solution seems more certain. To elaborate, in electrolytic deposition of germanium experiments, Papa et al. [22] found that up to 40 μm thick, void-free amorphous films of Ge are deposited on a Cu anode by electrolysis of 7% $GeCl_4$ solution in propylene glycol, using Ge as cathode [23]. (Ge is a metalloid whose electrical resistivity is ~1 Ω m at 293 K. Both amorphous and crystalline films of Ge deposited on a good conducting metal can be used as electrodes in $GeCl_4$ solution.) Deposition of amorphous Ge by electrolysis of a $GeCl_4$ solution using a Ge cathode seems to be an evidence that free energy of an amorphous solid is greater than of the crystal. How much greater it is can only be determined from calorimetric measurements on amorphous Ge and the standard emf of its electrolytic cell. We also suggest that glassy and crystalline solids of binary and multi-component alloys may be used as electrodes in an ionic solution of their one component. In that case their partial molar free energies would become relevant.

As noted earlier here, non-crystalline solids are prepared by vapor deposition, chemical reaction, lyophilization, high-energy ball milling of crystals, collapse of crystals at high pressures, and by high-energy irradiation of crystalline metal and other solids. According to the Boltzmann equation and the entropy-loss view, their S_{conf} and S_{res} would decrease to zero also but abruptly. Since the excess free energy of these solids would be high, a galvanic cell constructed with one electrode made from such a solid and the other made from a crystalline solid would produce a relatively high emf. If the value of ΔG_{exc} estimated from this emf is found to be close to the value deduced by using the Boltzmann's statistics, on which the entropy-loss view is based, the inference that a glass has no residual entropy would prevail, otherwise it would not.

7. Concluding remarks

By using experiments to measure the free energy change directly, one may be able to determine whether or not the configurational entropy of a liquid vanishes on vitrification. Such experiments require measuring the vapor pressure, evaporation rate, solubility ratio, chemical reaction rate, and emf of an electrolytic cell containing electrodes made from glassy and other non-crystalline solids. These experiments would also yield useful information on the roles of calorimetric and statistical entropies, and the resulting discussion would bear upon our understanding of the term Ω in the Boltzmann equation. Electrolytic deposition of amorphous germanium on anode from a Ge cathode immersed in $GeCl_4$ solution shows that thermodynamic relations may be valid for phenomena involving non-equilibrium solids.

In the entropy-loss view, structural relaxation on annealing of a glass would first increase its entropy and then decrease it to its equilibrium value, thus showing a broad peak in the plot of its entropy against time. As a consequence, its free energy plot against time would show a decrease in slope at a certain time. This change also may be investigated by measuring the properties discussed above.

The data for examining the validity of the entropy-loss view are scarce in the literature. Even the ones that can be used had been obtained from experiments for a different purpose, and therefore their use is limited here. Nevertheless, analysis of such data provides no support for the view that the residual entropy of glass may be zero, as was recently discussed by Nemilov [23] in his analysis and discussion of the third law. We hope that more experiments will be performed to test the known consequences of the entropy-loss view and new consequences will be reported, and tested by experiments.

As mentioned earlier here, a one-dimensional model simulation of glass transition has produced a sigmoid shape decrease in S_{exc} on cooling that corresponds to a lambda-type change in the specific heat and either a monotonic or non-monotonic increase in S_{exc} and a corresponding decrease in G_{exc} with time on structural relaxation [2]. Gujrati [24] has concluded that there are certain fundamental problems in the computational simulation of the entropy in Ref. [2]. These prevent us from relating the simulations directly to the Kivelson and Reiss [1] arguments for the entropy loss view.

References

[1] D. Kivelson, H. Reiss, J. Phys. Chem. B 103 (1999) 8337.

[2] P.K. Gupta, J.C. Mauro, J. Chem. Phys. 126 (2007) 224504. They supported the Kivelson-Reiss arguments, by a highly simplified simulation in one-dimensional enthalpy landscape model, and obtained sigmoid-shape plots of S_{conf} against T, which yield a lambda-like shape of the specific heat, $C_p[(\mathrm{d}S/\mathrm{d}T)_p = C_p/T]$, contrary to the characteristic sigmoid-shape rise in C_p. Moreover, lack of resemblance of their simulated plots of the free energy and observed plots would prevent one from further considering their view, although we have included those here. See also, arXiv:0909.0238v1 [cond-mat.dis-nn], arXiv:0909.0734v1 [cond-mat.dis-nn].

[3] M. Goldstein, J. Chem. Phys. 128 (2008) 154510.

[4] J.W.P. Schmelzer, I. Gutzow, J. Non-Cryst. Solids 355 (2009) 581.

[5] H. Reiss, J. Non-Cryst. Solids 355 (2009) 617.

[6] G.W. Scherer, Relaxation in Glass and Composites, Wiley, NY, 1986.

[7] S. Nemilov, Thermodynamics and Kinetic Aspects of the Vitreous State, CRC Press, Boca Raton, 1995.

[8] I. Gutzow, J. Schmelzer, The Vitreous State: Thermodynamics, Structure. Rheology and Crystallization, Springer, Heidelberg, 1995.

[9] E. Donth, The Glass Transition: Relaxation Dynamics in Liquids and Disordered Materials, Springer, Berlin, 2001.

[10] G.P. Johari, J. Chem. Phys. 112 (2000) 7518.

[11] T. Hikima, N. Okomoto, M. Hanaya, M. Oguni, J. Chem. Thermodyn. 30 (1998) 509.

[12] G.P. Johari, J. Chem. Phys. 113 (2000) 751.

[13] R.J. Speedy, P.G. Debenedetti, R.S. Smith, C. Huang, B.D. Kay, J. Chem. Phys. 105 (1996) 240.

[14] A. Kouchi, T. Kuroda, Jpn. J. Appl. Phys. 29 (1990) 807.

[15] G.N. Papatheodorou, S.A. Solin, Phys. Rev. B 13 (1976) 1741.

[16] E. Grantcharova, I. Gutzow, J. Non-Cryst. Solids 81 (1986) 99.

[17] B.C. Hancock, M. Parks, Pharm. Res. 17 (2000) 397.

[18] K. Überreiter, W. Bruns, Ber. Bunsengesselschaft Physikalische Chemie 68 (1964) 541;
K. Überreiter, W. Bruns, Ber. Bunsengesselschaft Physikalische Chemie 70 (1966) 17, See also Fig. 3.14, Chapter 3, p. 108 in Ref. [8].

[19] M. Barcea, B.A. Wolfe, J. Chem. Phys. 124 (2006) 174902.

[20] C. Bergman, R. Chastel, J. Phys. (Coll. 9) 43 (1982) 199.

[21] R.A. Swalin, Thermodynamics of Solids, Wiley–Interscience, 1972.

[22] T. Papa, D. Sette, L. Stagni, J. Phys. D: Appl. Phys. 7 (1974) 2024.

[23] S.V. Nemilov, J. Non-Cryst. Solids 355 (2009) 607.

[24] P. D. Gujrati, arXiv:0909.0238v1 [cond-mat.dis-nn], arXiv:0909.0734v1 [cond-mat.dis-nn] and, arXiv:0910.0026v1. [cond-mat.stat-mech].