



Specific heat relaxation-based critique of isothermal glass transition, zero residual entropy and time-average formalism for ergodicity loss

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ABSTRACT

In support of the view that entropy is lost on glass formation, the C_p relaxation spectra were regarded as experimental proof of time- and temperature-dependent loss of both ergodicity and entropy, and confirmation of isothermal glass transition. Also, both $C_p \rightarrow 0$ and $S \rightarrow 0$ in the limits of $t_{\text{obs}} \rightarrow 0$ s, and $T \rightarrow 0$ K were cited as further proof. We found no experimental evidence in support of the view. A critical examination shows that the C_p and C_p' spectra used to reach these conclusions indicate phase-lag between the response and perturbation, not loss of ergodicity or loss of configurational degrees of freedom, and $C_p \rightarrow 0$ as $T \rightarrow 0$ K is not evidence for $S \rightarrow 0$ as $T \rightarrow 0$ K. The notions of partial ergodicity and entropy and their dependence on t_{obs} are inconsistent with the properties measured during cooling, heating and isothermal annealing, and thermodynamic consequences of the apparent proof are untenable. The premise that glass formation is a process of continuously breaking ergodicity with entropy loss does not merit serious consideration.

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1. Introduction

Tammann [1] recognized that liquid to glass transformation occurs over a narrow range of temperature. In 1931, Thomas and Parks [2] showed that the specific heat, C_p , of B_2O_3 measured on the cooling path from liquid to glass differs from that measured on the heating path from glass to liquid. The resulting shape and magnitude of the hysteresis loop in C_p and in all other properties depend upon the time scale of an experiment and the annealing conditions of glass, indicating an occurrence of spontaneous process. The consequent irreversibility of properties measured in the liquid–glass transition range is recognized as a characteristic feature of glass formation [3–18]; it forbids one from determining the entropy change from the $C_p \ln T$ integral. Nevertheless, studies [7,12–15] have shown that despite that the $C_p \ln T$ integral yields the same values on the heating and cooling paths within experimental errors as long as all isothermal annealing effects are taken into account. Also, the fictive temperature, T_f , has been determined from the $C_p \ln T$ integral for hyperquenched glasses, which show a large enthalpy loss on heating. Its value was found to be only slightly different from the value of T_f determined from the $C_p dT$ integral [16]. A recently revived notion that residual entropy of glass may be an artifact of using equilibrium thermodynamics relations for liquid–glass transition [17] has been critically examined in

several studies [10,13,18–22]. In this paper, we examine the notion of partial ergodicity and its loss that has been used to support this notion [17].

To review briefly, the concept of *Ergodenhypothese* used by Boltzmann in his papers on kinetic theory of gases has been used for condensed disordered systems, including spin glasses. It postulates that all microstates in phase space corresponding to the surface of constant energy are equally probable and can be (and are) accessed over a sufficiently long period of time. An ergodic system is defined as one in which the time-average of every measurable property gives the same result as the corresponding ensemble average, and a non-ergodic system as one in which it does not. No intermediate system state and partial ergodicity were defined. In statistical terms, a system is seen as ergodic if it visits with equal probability all possible microstates consistent with a specific macrostate over an unspecified period of time. It is seen as non-ergodic if it does not. In the use of this hypothesis, each distinct component of the partitioned (configurational) phase space is seen as an enthalpy basin (microstates), for which hypothetical conditions of internal ergodicity are obeyed. In seeking its relevance to glass formation, Palmer [23] considered the case of *discontinuously* broken ergodicity or *discontinuous* loss of ergodic behavior; a liquid being ergodic and a glass non-ergodic. In discussing experimental and statistical entropies, Jäckle [24] examined Palmer's view and pointed out that existence of two alternative formulations of statistical mechanics, one producing residual entropy and other not, is characteristic for a non-ergodic system. For considering the residual entropy of glass, he preferred to retain the statistical mechanics

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in unmodified form. In an experimental context of the relaxation spectra, Angell [25] took the view that a crossover between ergodic and non-ergodic behavior occurs when the condition $\omega\tau = 1$ is met where τ is the characteristic relaxation time and ω the angular frequency at which the loss observed is maximum. This corresponds to the condition $D = 1$ when one defines $D = \tau/t_{\text{obs}}$, with τ as internal time and $t_{\text{obs}} = 1/\omega$ as the external or observation time. The behavior is ergodic for $D < 1$, i.e., equilibration occurs much faster than the time it takes to perform a measurement, and nonergodic for $D > 1$.

In support of the view that configurational entropy, S_{conf} , may be almost all lost on glass formation and a glass may not have residual entropy [17], Mauro et al. modified Palmer's original approach to their own view of continuously broken ergodicity (continuous loss of ergodic behavior), which they called a "notion", "framework" and "theory" in Ref. [26]. The modification had the effect of broadening the temperature range of liquid–glass transition by an unusually large amount, and it apparently justified the view that a time average formalism is essential for accounting the presumed dependence of thermodynamic properties on t_{obs} [26]. Thus, they concluded [26], "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." In relating it to specific heat spectroscopy, they took the time duration for observation, $t_{\text{obs}} = 1/\nu$, where $\nu (= \omega/2\pi)$ is the temperature perturbation frequency in Hz, and argued that the number of microstates explored by a system decreases as t_{obs} is decreased by increasing ν . Thus the decrease in C_p' with increasing ν in the spectra was seen as evidence for continuous breakdown of ergodicity resulting from freezing of configurational degrees of freedom, and the C_p' spectra itself was seen as confirmation of isothermal glass transition. (Here, C_p' is the real, in-phase or storage component of the complex specific heat, $C_p^* = C_p' - iC_p''$, where C_p'' is the imaginary, out of phase or loss component. For convenience, hereafter we refer to loss of configurational degrees of freedom as kinetic freezing.) They also concluded that both the entropy $S \rightarrow 0$ and $C_p \rightarrow 0$ in the limits of $t_{\text{obs}} \rightarrow 0$ s and $T \rightarrow 0$ K, and cited these as experimental proof of their analysis [26]: "Our analysis demonstrates that a time-average formalism is essential to account correctly for the experimentally observed dependence of thermodynamic properties on observation time, e.g., in specific heat spectroscopy. This result serves as experimental and theoretical proof for the nonexistence of residual glass entropy at absolute zero temperature." Finally, they wrote [26]: "As we have already discussed, the experimental evidence for the validity of the time average is overwhelming and can leave no doubt about this conclusion. We emphasize that this is not a matter of interpretation or personal preference, as some would claim, but rather a matter of experimental fact."

There were arguments already against the view that glass may have no residual entropy. Kivelson and Reiss arguments [17] in its favor led to new calorimetric experiments, which showed that their arguments against the reality of residual entropy cannot be sustained [11–16]. Here we first critically examine Mauro et al.'s [26] experimental proof in support of Kivelson and Reiss view. We find that decrease in C_p' with increasing ν was incorrectly interpreted as "freezing" or "loss" of the configurational degrees of freedom at "short observation times" corresponding to the $t_{\text{obs}} = 1/\nu$, and the C_p' spectra do not indicate isothermal change in S_{conf} or liquid–glass transition reversibly. Moreover, experiments have always shown that $C_p \rightarrow 0$ as $T \rightarrow 0$ K for all glasses of all thermal histories. Therefore, $C_p \rightarrow 0$ as $T \rightarrow 0$ K is not a proof for $S \rightarrow 0$ as $T \rightarrow 0$ K. After discussing several thermodynamic consequences of their notion [26], we conclude that there is no experimental evidence for superiority of their time average formalism over the ensemble average formalism for thermodynamic properties. Therefore, it does not seem meaningful to describe glass formation as a process of con-

tinuously broken ergodicity with loss of entropy. A critique of their interpretation of C_p relaxation spectra was given in a Comment, and they provided a reply [27]. Both may be consulted. We also provide an analysis of their view of partial ergodicity and entropy loss and include more details and critical discussion.

2. Specific heat spectra, freezing of configurational degrees of freedom and entropy

In relaxation spectroscopy, a perturbation from equilibrium biases random fluctuations in the direction of perturbation, and thus reveals the dynamics of already occurring Brownian (molecular) motions. Change in the structure on the characteristic time of perturbation is negligibly small. When there is a phase lag between the response and perturbation one observes the real and imaginary components of complex susceptibility and a finite loss tangent. Analysis of relaxation spectra yields the distribution of relaxation times β , the amplitude of dispersion and characteristic relaxation time τ .

Theoretical basis of specific heat spectroscopy and details of data analysis and interpretation are well established, although less widely known. These are given in Refs. [28–41]. Briefly, when there is a phase lag between heat oscillation and temperature oscillation, C_p' decreases with increase in ν continuously from $C_{p,0}$ at $\omega\tau \ll 1$ toward $C_{p,\infty}$ at $\omega\tau \gg 1$, where $C_{p,0}$ and $C_{p,\infty}$ are, respectively, the relaxed and unrelaxed values of C_p . The decrease occurs according to an inverted, stretched sigmoid-shape curve and C_p'' shows a peak at frequency $\omega = 1/\tau$. Phenomenologically, $C_p' \rightarrow C_{p,0}$ and $C_p'' \rightarrow 0$ in the limits $\omega\tau \rightarrow 0$, and $C_p' \rightarrow C_{p,\infty}$ and $C_p'' \rightarrow 0$ in the limits $\omega\tau \rightarrow \infty$. Distribution of relaxation times and occurrence of faster relaxation of the JG-type also prevent one from approaching close to $C_{p,\infty}$ value. Relaxation spectra neither give information on glass formation nor yield T_g .

Mauro et al. wrote [26]: "The theory of continuously broken ergodicity is supported by a number of experiments, particularly the specific heat spectroscopy experiments pioneered by Birge and Nagel⁴⁰, in which the heat capacity of a liquid is measured over a wide range of frequencies. Birge and Nagel clearly show that liquids undergo a continuous loss of their configurational degrees of freedom at higher frequencies. Since observation time is inversely proportional to the measurement frequency, the experiments of Birge and Nagel are a beautiful example of an *isothermal glass transition* purely induced by changes in the observation time. Without altering the temperature of a liquid, it undergoes a continuous glass transition (i.e., a continuous loss of ergodicity) simply by decreasing the observation time (i.e., increasing the measurement frequency). As with a "standard" glass transition (i.e., by changing temperature at a fixed observation time), the breakdown of ergodicity is accompanied by a loss of the configurational degrees of freedom, which manifests itself as a loss of configurational heat capacity." Since they [26] did not mention C_p'' , it is unclear whether the distinction between C_p' and C_p , and importance of the loss component were appreciated. To further justify their notion, they wrote [26], "The zero entropy obtained in the two limiting cases of $t \rightarrow 0$ and $T \rightarrow 0$ is in agreement with Boltzmann's notion of entropy as the number of constituent microstates that are visited to yield a given macrostate." It is obvious that less and less of an occurrence would be observed in the limit $t \rightarrow 0$ and ultimately nothing would be observed. In a relaxation experiment, the lower limit of t_{obs} is 1 ps (ν is ~ 1 THz), therefore we use the limits $C_p' \rightarrow C_{p,\infty}$, and $S_{\text{conf}} \rightarrow 0$.

In Angell's [25] view, the behavior would be ergodic at $\nu < \nu_{\text{peak}}$ (ν_{peak} is the frequency at which the C_p'' peak appears), and non-ergodic at $\nu > \nu_{\text{peak}}$. At the ergodic to non-ergodic transition, C_p' would be equal to $C_p'(\nu_{\text{peak}})$, the value of C_p' at ν_{peak} . Regardless of the distribution of relaxation times, C_p' would be between $C_{p,0}$

and $C_p'(v_{\text{peak}})$ for the ergodic state and between $C_{p,\infty}$ and $C_p'(v_{\text{peak}})$ for the non-ergodic state. This conflicts with the use of C_p' spectra as evidence for continuous glass transition and ergodicity breaking in Ref. [26], because in this case C_p' would be equal to $C_{p,0}$ for the ergodic state and equal to $C_{p,\infty}$ for the non-ergodic state. If S_{conf} were to decrease with increase in v , the shape of the S_{conf} against $\log(v)$ plot would resemble the C_p' spectra. But the sigmoid shapes of both S_{conf} and C_p' plots against $\log(t_{\text{obs}})$ would not resemble the shape of a DSC scan observed on heating a glass through the glass–liquid transition range during which enthalpy relaxation and recovery occur. Since only small parts of phase space are explored in any reasonable observation time at any temperature, it is doubtful that a transition to a truly ergodic state occurs.

Birge and Nagel [28], Birge [29] and others [30–34,36–42] had described the C_p' and C_p'' spectra already in terms of generally known perturbation and had shown that C_p' and C_p'' follow the Kramers–Kronig relations in a linear response theory and are consistent with the fluctuation–dissipation theorem for susceptibility. Numerous comparisons of the specific heat, dielectric and ultrasonic relaxation spectroscopy results by others [36,37] have confirmed their conclusions [28,29]. But, Mauro et al. [26,27] interpreted Birge and Nagel's study as an experiment for observing structural freezing and unfreezing, and disregarded the significance of C_p' and the loss tangent, $\tan \delta (= C_p''/C_p')$ while asserting that (i) the C_p' spectra shows a continuous loss of C_p and S_{conf} with decreasing t_{obs} , (ii) the C_p' spectra is a feature of isothermally occurring glass transition, and (iii) the decrease in C_p' , the loss of ergodic behavior and of S_{conf} , the liquid–glass transition and attainment of an apparently non-equilibrium state by cooling and/or reducing t_{obs} are manifestations of the same occurrence. Those who are aware of Birge and Nagel and others [30–34,36–42] analyses of the C_p' and C_p'' spectra for obtaining β and τ , and comparison of the results obtained against other spectroscopy results would be surprised by the assertion [26]: “Thus, application of ergodic statistical mechanics cannot account for the dependence of heat capacity on observation time, an experimentally proven effect determined by Birge and Nagel.”

Studies of molecular relaxation by dielectric spectroscopy since the 1920s [43] have emphasized both the purpose and significance of using small perturbations from equilibrium, as have the studies by specific heat spectroscopy since the 1980s [28–34,36–42]. They have also stressed the need for maintaining a distinction between relaxation measurements in equilibrium and those in the irreversible region of glass transition. Therefore, a discussion of the conditions for kinetic freezing in terms of D , the ratio of the internal time (of structural fluctuations) and external time (duration of observation or measurement) would seem unnecessary here. Nevertheless, we make two observations on the use of the relation $D = \tau/t_{\text{obs}}$ for instructive purposes: (i) In the original definition of D , t_{obs} is the time duration of an observation *without perturbing* the state of the system, e.g., exposure time of a camera lens for photographing a moving object), and, (ii) if one extends the definition of $D = \tau/t_{\text{obs}}$ by using $t_{\text{obs}} = 1/\omega$ in a spectra by accepting the condition for kinetic freezing defined by $\tau/t_{\text{obs}} = 1$ or $D = 1$, then kinetic freezing would occur at $\omega\tau = 1$, which is a condition for which C_p'' peak appears. The C_p'' peak's frequency would divide the spectra into two regions, one on its left ($\omega\tau < 1$) in which the state for all t_{obs} defined by ω is liquid and second on its right ($\omega\tau > 1$) in which the state is kinetically frozen for all t_{obs} defined also by ω . In describing the crossover between ergodic and non-ergodic behavior as equivalent to isothermal glass transition, Angell [25] used $D = 1$ or $\omega\tau = 1$ as an argument based on dielectric relaxation studies. This is strange because it means that for all temperatures, however high, crossover of ergodic to non-ergodic behavior would always occur when the maximum loss condition is reached. For temperature and pressure conditions of $\tau = 100$ s, isothermal spectra would

show a glass transition at $\omega = 10$ mrad/s according to Angell [25], even though the perturbation only serves to bias the direction of already occurring random diffusion (and thereby reveals the existence of molecular motions). In some interpretations, distribution of relaxation times is described in terms of multiplicity of Debye-type single relaxation times, τ_{Debye} . In such a case also, there would be no ω at which the behavior would be ergodic – there would always be some kinetically frozen modes at the lowest ω (longest t_{obs}). Accordingly, even the behavior of a liquid is expected to be formally non-ergodic.

It is also instructive to note that kinetic freezing and unfreezing may occur within one ω -cycle for certain conditions. This was the basis for Simon and McKenna's interpretation [35] of Birge and Nagel's studies [28,29] and the suggestion of a frequency-dependent fictive temperature, which Mauro et al. [26] called isothermal glass transition. But a property measured on the kinetic freezing path differs from that measured on the unfreezing path. To maintain distinction between the effects of cooling and heating and the effects of perturbation, here we use the terms “ $C_p' - v$ and $C_p'' - v$ plots” when kinetic freezing and unfreezing occur, and the term “ C_p' and C_p'' spectra” for the relaxation spectra. Since their distinctive features are not widely known, we list these:

- (i) The C_p' and C_p'' spectra obey the Kramers–Kronig relation and are consistent with the fluctuation dissipation theorem, but not the $C_p' - v$ and $C_p'' - v$ plots.
- (ii) C_p' and C_p'' spectra measured on the cooling path are the same as on the heating path within an ω -cycle but the $C_p' - v$ and $C_p'' - v$ plots are not.
- (iii) A relaxation spectrum is Fourier transform of a step-function response that is described by the Maxwell–Voigt elements, i.e., linear combinations of spring and dashpots. Changes observed on kinetic freezing and unfreezing, if introduced in the Kelvin–Voigt model, would not yield spectra on Fourier transform or else be analyzable as spectra.
- (iv) A peak in C_p'' spectra appears and its values is used together with C_p' to determine τ , β , $C_{p,0}$ and $C_{p,\infty}$, but no such peak has been observed in the $C_p'' - v$ plot.
- (v) Increase in ω from $\omega\tau \ll 1$ to $\omega\tau \gg 1$ condition decreases $C_p' \approx C_{p,0}$, to $C_p' \approx C_{p,\infty}$ in the spectra, but would decrease $C_p' \approx C_{p,0}$ to $C_p' \approx C_{p,\text{glass}}$ in the $C_p' - v$ plot.

In summary, C_p' and C_p'' spectra do not indicate freezing of configurational degrees of freedom, breakdown of ergodicity or glass formation.

One also studies the features of C_p' and C_p'' isochrones, i.e., plots of C_p' and C_p'' for a fixed v against T measured during the cooling and heating a material at rate q . These show features due to relaxation as well as kinetic freezing and unfreezing. In addition, they show variation in C_p of the glassy state with T .

- (i) Relaxation of C_p' in an isochrone appears as a sigmoid shape variation and of C_p'' as a peak at a characteristic T when $\omega\tau = 1$, the state remains at equilibrium with changing T where free energy is a minimum. C_p' and C_p'' measured on the heating path are the same as those measured on the cooling path. Their temperature range does not vary with q . When experiments are performed for a lower ω , the C_p' and C_p'' relaxation features shift to lower T .
- (ii) In the temperature range of kinetic freezing/unfreezing, a C_p' isochrone shows features similar to those of a DSC scan, i.e., the values measured on the cooling path differ from those measured on the heating path and the plot obtained on cooling crosses the plot obtained on heating and the latter shows an endothermic overshoot. Their temperature range varies with

- q . When q is decreased, the features shifts to lower T and lower C_p range and become almost undetectable when q is very small.
- (iii) $C_{p,\text{glass}}$ formed is higher than $C_{p,\infty}$ of the liquid extrapolated to $T < T_g$ and its value decreases spontaneously to $C_{p,\infty}$ with the clock-time.

It is well recognized that external perturbation by an electric field (or mechanical deformation) in dielectric (or mechanical) relaxation studies means that more electrical (or elastic) dipoles on the average are aligned in the direction of the electric (or mechanical stress) field than in the opposite direction while still undergoing translational and rotational diffusion. It does *not* mean that Brownian motion of some of the molecules has become kinetically frozen. It is strange that unlike the original authors [28,29], Mauro et al. [26,27] treated external perturbations like temperature oscillations equivalent to the cooling rates during kinetic freezing, and compared them both with the internal time scale of Brownian diffusion in the system. One cannot escape the conclusion that decreases in C_p as “proof” [26] for loss of configurational C_p , S_{conf} and ergodicity on the time scale of ν was based on misinterpretation of the spectra.

3. The specific heat spectra, entropy and free energy

In fairness to the efforts of Mauro et al. [26], we assume temporarily that C_p spectra indicate decrease in S_{conf} with increase in ν , and inquire what consequences it would have for measurable properties of a glass.

First we consider the configurational free energy, $G_{\text{conf}} = H_{\text{conf}} - T S_{\text{conf}}$. A decrease in S_{conf} with increase in ν [26] would increase G_{conf} measured on the time scale of ν , and increase in S_{conf} with decrease in ν would decrease it, i.e., G_{conf} would reversibly change with the time scale of ν whether or not H_{conf} changes in the liquid–glass range. Therefore, if the plot of S_{conf} against $\log(\nu)$ resembles the C_p' spectra, the plot of G_{conf} against $\log(1/\nu)$ would resemble the C_p' spectra. At $t_{\text{obs}} (= 1/\nu)$ corresponding to lowest ν , S_{conf} is highest and G_{conf} would be minimum, and at t_{obs} corresponding to highest ν , S_{conf} is close to zero and G_{conf} would be close to H_{conf} . Solubility, vapor pressure and chemical reactivity of a material are proportional to the exponential of free energy divided by RT , and therefore magnitude of these properties would depend upon ν or t_{obs} . If we switch the perturbation of the system from very low ν to a high ν , magnitude of these properties *measured* on the time scale of ν would increase by a large amount. When observed for a short duration at a fixed T , the state would be found to be greatly more soluble, vaporizable and reactive, and when observed for a long duration the state would be much less so. But solubility, vapor pressure and chemical reactivity do not depend upon one's time for observation unless one assumes that the equilibrium constant varies with time. If C_p' spectra were to truly indicate loss of S_{conf} , one could vary ν (or t_{obs}) between say 1 Hz and 0.1 mHz (or 1 s and 10 ks on a clock-time) and find that the properties have different magnitudes for different t_{obs} . If such a difference were to occur, it could be used to improve a technological process. We found no studies indicating that the vapor pressure, solubility, chemical reactivity, etc., decrease when t_{obs} is decreased.

Second, we would not be able to use the $C_p'' - \nu$ plot to obtain τ , β , $C_{p,0}$ and $C_{p,\infty}$ of a liquid. Last, since there is no loss of enthalpy [17,18,26] on increasing ν , we would have to disregard our understanding of C_p'' as a measure of loss of energy. To elaborate, the imaginary or loss component χ'' generally determines dissipation of energy per cycle of frequency, and is given by, $\Delta W = \pi\phi\chi''$, where ϕ is the amplitude of perturbation [43]. In specific heat relaxation, $\Delta W = \pi\delta T C_p''$, where δT is the amplitude of temperature oscillation. In its discussion, Höhne [44] argued that this may also be

the case for C_p'' and he showed it to be so by using the area of the ellipse obtained by plotting the temperature against heat exchange in one ω -cycle. Depending upon the distance of the pathway from equilibrium, there would also be an entropy production. Others have suggested that there is only an entropy change given by, $\delta S = \pi C_p'' (\delta T/T)$ [36]. (Note that Höhne's objection against the validity of the relation for the entropy exchanged per cycle on the basis of the Clausius inequality may be less serious in practical terms because the entropy change on the irreversible cooling and heating paths in the glass formation range is found to be negligibly small [12–16].) Since the δT perturbation is small, ΔW in units of Joules is negligible and any heat generated disappears in an isothermal experiment. But when C_p'' is maximum for a certain ω , T condition, increasing δT would cause it to dissipate more heat. This means that for ω , T condition of the C_p'' peak, at which $t_{\text{obs}} = \tau$, the C_p' and C_p'' values would correspond to a finite S_{conf} while the liquid is dissipating energy. As heat is dissipated at each ν , the presumed decrease in S_{conf} on increasing ν would not be occurring in a process in which the system is passive. One cannot ignore the C_p'' spectra and its origin when interpreting the C_p' spectra as an indication of decrease in S_{conf} on loss of configurational degrees of freedom by kinetic freezing.

4. Specific heat in TMDSC and the entropy

Temperature modulated differential scanning calorimetry (TMDSC) provides isochrones containing features of both the relaxation and liquid–glass transition. Relaxation features appear at high temperatures and liquid–glass transition features at low temperatures [32–34,36–40,42,46–49,8,50,51]. Variation of C_p' and C_p'' in TMDSC isochrones has been discussed by several groups, who compared the isochrones against the DSC scans for the same q and used the isochrones for studying the dynamic behavior of liquids, reaction kinetics and reversible and irreversible phase transformations [33,37,39,40,45–49,8,50,51]. Briefly, as τ varies with T and the liquid remains in internal equilibrium, the term $\omega\tau$ varies in the range $\omega\tau \ll 1$ and $\omega\tau \gg 1$. The phase-lag between heat oscillation and temperature oscillation causes C_p' to (reversibly) vary in a sigmoid shape manner with T , while C_p'' shows a peak at temperature when $\tau = 1/\omega$ [32–42,45–49,8,50,51]. Changing q has no effect on these features as long as the time scale corresponding to q does not become comparable to τ and the features characteristically appear at temperatures higher than those of the DSC scan for the same q . Their shapes vary according to the sensitivity of τ to T , contributions from the JG relaxation, the parameter β and variation in $C_{p,0}$ and $C_{p,\infty}$ with T . When a higher ω is used, the features shift to higher T and, although they are due to occurrence of the α -relaxation process, they have been occasionally referred to as dynamic glass transition in response to temperature oscillation [39,40]. The integral of $C_p' dT$ does not yield the enthalpy difference between two temperatures.

Kinetic freezing/unfreezing are observable in a TMDSC isochrone for all values of q and ω but in different temperature ranges and the C_p' features resemble the DSC scan, i.e., (i) the cooling and heating isochrones cross each other, (ii) an overshoot appears in the heating isochrone before the equilibrium state is reached, (iii) C_p' measured on the cooling path differs from that measured on the heating path, (iv) the characteristic time for kinetic freezing/unfreezing at any instant in the path-irreversible temperature range differs from τ and (v) decrease in q shifts the features to a lower T range where C_p' of the liquid is closer to its temperature-dependent $C_{p,\infty}$, the features of kinetic freezing/unfreezing at very low q can be observed only when C_p' data are extremely accurate (see Refs. [39,40] and the plots in Fig. 1 in Ref. [49]) and corresponding change in the slope of the C_p'' isochrone is rarely observed

because the C_p'' value is usually too low. Also, the temperature range over which the features appear is narrower for low q than for high q . In contrast, increase in q shifts the features to a higher T range where their magnitude is higher and they more clearly overlap the features of C_p' relaxation, making them appear increasingly more like a DSC scan. The underlying relaxation is still indicated by the simultaneously measured C_p'' whose peak height differs on the cooling and heating paths when kinetic freezing/unfreezing features overlap the relaxation features. It is to be noted that these observations have been used to clarify [32–42,45–49,8,50,51] an alternative interpretation of the C_p' and C_p'' spectra that were analyzed in terms of the Tool–Narayanaswamy–Moynihan model with a (path irreversibility-determining) nonlinearity parameter and an Arrhenius relaxation time-dependence [35].

The features of kinetic freezing/unfreezing show that although relaxation decreases C_p' on cooling, the liquid does not lose S_{conf} when cooled through the relaxation range. $C_{p,\text{glass}}$ is higher than the extrapolated $C_{p,\infty}$ of liquid and its value decreases with the clock time. The $C_p' dT$ and $C_p' \ln T$ integrals measured in TMDSC do not yield changes in the enthalpy or entropy; only the $C_p dT$ and $C_p \ln T$ integrals measured in DSC yields these values. In summary, neither the C_p' and C_p'' spectra nor the isochrones indicate loss of S_{conf} in the relaxation process nor is the relaxation spectra be interpretable as isothermal glass transition.

We also note that temperature modulated dilatometry has been used by Bauer et al. [52] to investigate the α -relaxation process in three polymers by using capacitance scanning technique. In their measurements thermal expansion coefficient, α_p appears as complex susceptibility, $\alpha_p^*(\omega) = \alpha_p'(\omega) - i\alpha_p''(\omega)$, where α_p' and α_p'' are the real and imaginary components of α_p^* , consistent with the fluctuation-dissipation theorem. The study, which is analogous to TMDSC, showed that in the isochrones, α_p' varies in a manner analogous to C_p' , and α_p'' shows a peak similar to the C_p'' peak when T is such that $\omega\tau = 1$. Both the α_p' and α_p'' features shifted to lower T as ω were decreased [52]. The features appeared *not* because of breakdown of ergodicity resulting from freezing of configurational degrees of freedom, but because of the phase lag between perturbation and response which increased. They also calculated τ and β of the polymers from their α_p' and α_p'' isochrones and found that both τ and β were consistent with the values measured from dielectric relaxation studies [52].

5. Change in entropy on thermal cycling, annealing, and apparent ergodicity restoration

As described in detail previously [15], Bestul and Chang [53], Goldstein [54], Langer and coworkers [55,56], and Sethna [57] showed that despite the irreversibility of the C_p values in the liquid–glass range, analysis of the data by using equilibrium thermodynamic relations shows that a glass has a residual entropy. Langer et al. [56] described their analysis as a theorem based on the second law of thermodynamics. We also note that Chow and Wu [58] independently deduced that there is a lower bound value for the residual entropy of a classical spin system, and showed it to be larger than zero. In response to a recently resurrected view [17] that a glass has no residual entropy, several authors gave new arguments and showed experimental evidence against it [10,59,60]. They did experiments to determine the $C_p \ln T$ integral on the heating and cooling paths that intrinsically contain the effect of kinetic freezing and unfreezing and concluded that glass has a residual entropy S_{conf} [10,12–16,19–22]. In addition to his earlier arguments [10,60], Goldstein concluded that [59], “. . . a spontaneous vanishing of entropy on cooling a substance through a kinetic transition between ergodic and non-ergodic conditions would not only represent a violation of the second law of thermodynamics, but that this

violation is not a trivial one correctible by a minor reformulation of that law, but instead leads directly to the possibility of construction of a perpetual motion machine of the second kind.”

It has been asserted that the inverse of the glass transition is (spontaneous) structural relaxation, which involves restoration of ergodicity as a glass approaches the liquid state and structural relaxation must entail an increase in entropy [26]. The postulate is that when more time is allowed for annealing at a certain fixed T_{ann} , the system would explore more microstates, and hence S_{conf} would increase toward the equilibrium value, while the enthalpy and volume decrease. Since the Clausius inequality forbids one from estimating the entropy change in a spontaneous process, the measured decrease in C_p and enthalpy with time [46,50] cannot be used to estimate the change in S_{conf} . However, it is believed that after the equilibrium state has been reached by isothermal annealing, the postulated increase in S_{conf} can be determined by measuring C_p of that state and using the $C_p \ln T$ integral from T_{ann} to the freezing point. But in order to measure C_p of the equilibrium state at T_{ann} , one needs to measure the temperature rise after a heat input over a time period much longer than the annealing time, and during that long time period the equilibrium state would be reached even if no annealing were done. Therefore, one would not know if spontaneous relaxation during annealing at T_{ann} increased S_{conf} to the equilibrium value or decreased it to the equilibrium value. Unfortunately, previous discussion on the subject overlooked the fact that direction of change in S_{conf} cannot be determined *during* the course of increasing t_{obs} (or annealing time), and spontaneous change in S_{conf} on annealing a glass can be detected only by performing measurements of C_p over a time period so long that annealing time itself become irrelevant.

There is indirect evidence for decrease in the entropy on spontaneous relaxation of glass: (i) DSC experiments in which an isothermal annealing step was inserted between the cooling and heating of the sample [15] showed that while the cyclic integral of $C_p \ln T$ was close to zero without the annealing step, the cyclic integral of $C_p \ln T$ for a sample having gone through the annealing step was not. It became close to zero only when the heat loss during isothermal annealing was used, in violation of the Clausius equation, to estimate the entropy loss for taking into account [15]. (ii) $C_{p,\text{glass}}$ decreases on annealing at T_{ann} to $C_{p,\infty}$ of the liquid [46,50], and it has been found that when C_p of the annealed sample is measured between $T \rightarrow 0\text{K}$ and T just below T_{ann} , the entropy change determined from the $C_p \ln T$ integral is less than that determined for the un-annealed sample [54].

Decrease in S_{conf} on annealing is seen to be consistent with the enthalpy landscape model in which structural relaxation of glass ultimately shifts the state point to a deeper minimum (of lower enthalpy) with the result that probability of exploring other minima of equal depth decreases. Since a deeper minimum has a relatively higher curvature, the corresponding Debye (vibrational) frequency would be higher. Therefore, the high frequency elastic modulus of a sample would increase on annealing as the probability of the state exploring other minimum of the same height or S_{conf} decreases. Several experiments have shown that the high-frequency shear modulus [61,62] and related elastic moduli increase [62,63] on annealing of a glass. We also point out that an apparently ergodic state of a liquid has lower S_{conf} and higher vibrational frequencies when its density is high than when its density is low.

If spontaneous relaxation of a glass is seen as a process inverse of glass formation [26], and S_{conf} were to increase with t_{obs} [64] during the annealing, G_{conf} would decrease and the solubility, vapor pressure and chemical reactivity of a glass corresponding to the relevant t_{obs} would decrease by a relatively large amount. We have found no evidence for its occurrence [22]. Moreover, simulations in a simple, one-dimensional enthalpy landscape model showed [64] that S_{conf} of a glass increases during structural relaxation, reaches a

value above the equilibrium (liquid) state value and then decreases to S_{conf} of the equilibrium state (Fig. 2 in Ref. [64]). In as much as it is seen as an ergodicity restoring process, this means that ergodicity would exceed that of the liquid and then decrease to the liquid value, which seems unlikely. We conclude that there is no support for the notion that S_{conf} increases on spontaneous relaxation of glass.

By using computer simulation, it was also shown that S_{conf} decreases to zero in an exceptionally broad sigmoid shape manner when a liquid is cooled to the glassy state [64]. Dependence of the broadness and the T range on the cooling rate and irreversibility of increase in S_{conf} on heating from near zero to its original value, are not justifiably described by Palmer's [23] ergodicity breaking approach.

Lastly, Bouchaud [65] has argued "that ageing is related to ergodicity breaking", which is in contrast to the ergodicity-restoring notion [26,64]. He used a phenomenological model for the dynamics of disordered systems and postulated a broad, power law probability distribution of the lifetimes of the many metastable states in the potential energy landscape, and a broad distribution of relaxation times. For these conditions he showed that there is a weak ergodicity breaking on annealing of spin glasses, and also likely for polymer glasses. As decrease in ergodicity is qualitatively taken to mean decrease in S_{conf} , Bouchaud's analysis [65] contradicts the notion that S_{conf} increases on spontaneous relaxation during annealing.

6. Approach of specific heat to zero value

We now consider whether or not vanishing of the heat capacity implies the corresponding vanishing of the entropy at absolute zero. As an experimental proof for zero residual entropy of glass [26], it was argued that just as Birge and Nagel's observation [28] cannot be accounted for by ergodic statistical mechanics, their own view [26] of $S \rightarrow 0$ and $C_p \rightarrow 0$ in the limits of $t_{\text{obs}} \rightarrow 0$ and $T \rightarrow 0$ cannot be accounted for by ergodic statistical mechanics. But Birge and Nagel [28] observed the decrease in C_p' and a peak in the C_p' spectra, not a decrease in C_p , and contrary to the claim that $C_p \rightarrow 0$ as $T \rightarrow 0$ in the plot of C_p against T in Fig. 1 in Ref. [26], "...provides experimental proof that entropy of the glass is zero", Fig. 1 in Ref. [26] just shows what has always been known, i.e., that for all systems including glasses of all thermal histories the measured C_p decreases to zero as $T \rightarrow 0$ K. Goldstein [60] has provided further arguments against the use of $S \rightarrow 0$ and $C_p \rightarrow 0$ in the limits of $t_{\text{obs}} \rightarrow 0$ and $T \rightarrow 0$ that Mauro et al's [26] used as proof that the entropy of glass is zero.

7. Concluding remarks

In general, relaxation spectra neither indicate freezing of configurational degrees of freedom with increasing frequency of perturbation, nor are interpretable as isothermal glass transition with decrease in the entropy. Contrary to the claim made [26], the C_p' spectra does not serve as proof for loss of configurational C_p , S_{conf} and ergodicity on the time scale of $1/\nu$. It has been known for a long time that for every material $C_p \rightarrow 0$ in the limit of $T \rightarrow 0$ K and therefore, it is not a proof that $S \rightarrow 0$ in the limit of $T \rightarrow 0$ K. This invalidate the conclusion [26]: "As we have already discussed, the experimental evidence for the validity of the time average is overwhelming and can leave no doubt about this conclusion. We emphasize that this is not a matter of interpretation or personal preference, as some would claim, but rather a matter of experimental fact."

Unfortunately, Mauro et al. [26,27] treated the characteristic time scales of (small) external perturbations as if they are temperature oscillations corresponding to the cooling/heating rates that cause kinetic freezing/unfreezing, and they compared them both

with the internal time scale of the system while it is obvious that these two have to be distinguished and compared separately. Moreover, one is led to untenable situations when different definitions of the external time scale are used. There is a difference between our inability to observe the consequences of perturbations when the phase difference grows and Brownian diffusion occurs than when Brownian diffusion is kinetically frozen.

If the notion of continuously breaking ergodicity with loss of entropy were correct, solubility, vapor pressure and reactivity of a liquid would depend upon the time one takes to observe them. They would be higher when observed for a short time and lower when observed for a long time, and this has not been found. Annealing experiments cannot determine whether S_{conf} has ultimately increased to its equilibrium value or decreased to the equilibrium value. Calorimetric studies performed by annealing a glass, and measurements of the high frequency shear modulus have shown that spontaneous relaxation decreases S_{conf} . Increase in S_{conf} above that of the liquid state value and then decreasing toward it, as observed in computer simulated isothermal annealing [64] are inconsistent with the premise that ergodicity cannot increase above its liquid state value.

We include below some general observations more by way of suggestions than conclusion, useful, perhaps, in framing issues that might enable one to use the ergodicity concept in relation to glass formation and its thermodynamics:

First: Palmer's [23] description of ergodicity originally intended as generalization of *broken symmetry* in spin glass systems has been used for liquid-glass transition. Since it is done without alternative descriptions or criticisms, we mention how some other authors have discussed Boltzmann's *Ergodenhypothese*. Based on his papers [66,67] about the kinetic theory of *gases*, it is a hypothesis that if a system is left to evolve freely and one waited for a long time, the system will pass through all the states consistent with its given value of the total energy. Its premise is that all accessible microstates are equally probable over a long period of time. It is also understood that for a system to be ergodic, the time-average response should be identical to the ensemble average response and fulfilling that condition requires that the phase point move over the entire potential energy hypersurface in a model of the energy landscape. But the time needed for a macroscopic system to explore the entirety of its own phase space is so long that, in a strict sense, no system, e.g., glycerol at ambient temperature, could be regarded as ergodic. Zermelo [68] has discussed the arguments used by Boltzmann in his *Ergodenhypothese*, pointing out that the concept that characteristic time needed for the phase points to pass sufficiently closely to all points in phase space ("recurrence times") is so large that it cannot have any relationship to the identity of time averaging and ensemble averaging, and there has also been a discussion of Poincaré recurrence theorem. In a related discussion of the necessity for enthalpy change in a process in which entropy changes, Gibbs [69] had already concluded that, "The impossibility of an uncompensated decrease of entropy seems to be reduced to an improbability".

In describing the relation of observational timescale, t_{obs} , with equilibrium in Section 2.1 of his paper, Palmer [23] used Feynman's words that in thermal equilibrium all the fast things have happened and all the slow things have not, and suggested that equilibrium depends crucially on t_{obs} which itself determines the meaning of 'fast' and 'slow', and different values of t_{obs} give different equilibria. Since this condition allows a system to reach equilibrium only in the limit $t_{\text{obs}} \rightarrow \infty$, equilibrium would never be reached in a real experiment, Palmer [23] reinterpreted the discussion in terms of ergodicity for spin glasses by assuming that t_{obs} "...is sufficient for the phase point to visit, not all of allowed phase space, but a sufficiently representative sample to give essentially the same results as for much longer time, even $t \rightarrow \infty$. The system is *effectively* ergodic."

We point out that a similar discussion appears in regard to the folding of a protein and its biological functions under the name of “the Levinthal paradox” and its resolution has involved no concept of ergodicity. The paradox is that finding the native folded state of a protein by a random search among all possible configurations would take a prohibitively long time, and yet proteins are observed to fold in a time period of seconds or less.

In the context of limitations of ergodic hypothesis, it is worth noting an occasionally given example of spontaneous magnetization in ferromagnetic systems, whereby at T below the Curie temperature the system preferentially adopts a non-zero magnetisation even though the ergodic hypothesis would imply that no net magnetisation should exist by virtue of the system exploring all states whose time-averaged magnetisation should be zero. A similar situation occurs for binary metal alloys at T a few degrees below their lambda-type disorder–order transition in which the system remains partially ordered even though partial order should not exist because vacancy and point defect diffusions are fast enough and the system can explore all states whose time-averaged order should be zero.

We also cite an analysis of ergodicity and its relation to statistical mechanics by Khinchin [70] in his 1949 book, which may be consulted, and we further draw attention to a comprehensive review of the foundation of ergodicity hypothesis, in which Badino wrote [71], “Above all, it must be said that Khinchin has the merit of having developed the statistical meaning of ergodicity and the relationships that exist between this and the laws of evolution of systems more than with the geometric structure of phase space.” Gujrati’s [72] has discussed some of these views, including the time-averaging and ensemble-averaging in stochastic and deterministic approaches. Goldstein [10,60] has argued that in view of the (at least) astronomically long time required for exploring the entire phase space, the assumption that the phase point can explore all possible configurations of equal energy is unrealistic and he resolved this issue by suggesting a different way of counting microstates [60]. In a general review of the liquid–glass transition, Dyre [73] pointed out that the liquid–glass transition has little in common with ergodic–nonergodic transitions of various lattice models, with the ideal mode-coupling theory, or with the jamming transitions of granular media.

Second: The notion of continuously broken ergodicity, originally restricted to laboratory glass transition [64], later included an *additional* “laboratory” glass transition occurring isothermally and reversibly with changing ω and expressed the quantity D in terms of ω . For this purpose Mauro et al. [26] used a discussion identical to the usual entropy discussion of systems described by a master equation, e.g., the H-theorem etc., although this was not made clear to the reader. While it was obvious that one observes less and less of any occurrence as $t_{\text{obs}} \rightarrow 0$, and nothing of an occurrence in the limits of $t_{\text{obs}} = 0$ or $\tau = \infty$, the use of such limits becomes meaningless in a laboratory time frame. Both partial ergodicity and its decrease as $t_{\text{obs}} \rightarrow 0$ deny the generally held view of ergodic and nonergodic behaviors, and there are questions as to whether equilibrium statistical mechanics involves ergodicity breaking.

Third: Bearing in mind that there is no experimental proof for partial ergodicity and time-dependent decrease in ergodicity and entropy – and there have been numerous objections [10–16,18–22,59,60] to these notions – it is worth inquiring what really led to these notions [26,27]: We find that the loss of ergodic behavior, the loss of S_{conf} and decrease in C_p , failure of a system to reach equilibrium, and the respective time and temperature-dependences of all were seen, first, as manifestations of the phenomena of liquid–glass transition [26,27]. Thereafter, all the preceding five manifestations were linked, (i) to the hypothesis that the state of a system is trapped in a specific description of configurational minimum in the potential energy landscape by using a

set of conditional probabilities, (ii) to an interpretation of ergodicity out of several disputed ones (some arguing that liquid–glass transition is not an ergodic to non-ergodic transition) and, (iii) to the view that the ratio D is equal to τ/t_{obs} with $t_{\text{obs}} = 1/\omega$, which is not the original definition of D , and ignoring the C_p'' peak. Finally, all five manifestations and three links were treated as self-evident [26,27], even though some arguments and experiments had denied their validity. There is need to verify these parts individually and in combination by experiment before using them to essentially support the Kivelson–Reiss view [17] of zero residual entropy. A framework of interwoven assertions, postulates and simple simulations is too fragile to sustain the notion of loss of entropy on glass formation.

Last, we note that the third law of thermodynamics was established by using the $C_p \ln T$ integral for crystals. However, a crystal does not exist in the ground state as $T \rightarrow 0\text{K}$; there is always kinetically frozen disorder in the lattice and hence there is a contribution to thermodynamic functions, albeit very small, from lattice defects. As pointed out earlier [16,74], crystals, like glasses, are in non-equilibrium state. Their properties spontaneously change with time until the equilibrium state is reached [74] and they show an irreversible path segment and almost indiscernible glass-like thermodynamics. Since our use of the $C_p \ln T$ integral for crystals is as inappropriate for determining the entropy change as the use of $C_p \ln T$ integral for glasses, we violate the Clausius inequality version of the second law in our attempt to establish the third law.

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