

Mechanical relaxation and the notion of time-dependent extent of ergodicity during the glass transition

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A postulate that ergodicity and entropy continuously decrease to zero on cooling a liquid to a glassy state was used to support the view that glass has *no* residual entropy, and the features of mechanical relaxation spectra were cited as proof for the decrease. We investigate whether such spectra and the relaxation isochrones can serve as the proof. We find that an increase in the *real component* of elastic moduli with an increase in spectral frequency does not indicate continuous loss of ergodicity and entropy, and the spectra do not confirm *isothermal* glass transition or loss of entropy. Variation in ergodicity and entropy with the spectral frequency has untenable consequences for both thermodynamics and molecular dynamics and implies that, despite a broad distribution of its relaxation times, an equilibrium liquid can be considered as always ergodic. Perturbation from equilibrium used to obtain a spectrum does not have the effect of dynamic freezing and unfreezing, and Maxwell-Voigt models for the mechanical response function have neither the characteristic irreversibility of liquid-glass transition nor are commutable to ergodicity or entropy.

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I. INTRODUCTION

The density time correlation function plays a central role in the dynamics of structural fluctuations and glass transition. It expresses the changes in both the characteristic relaxation time τ_0 of the viscosity-determining α -relaxation process and the relaxation time distribution parameter β with changing temperature T . When a liquid is cooled, density fluctuations in its structure become progressively slower until they dynamically freeze, and a glass, thus, forms. The freezing occurs [1] over a narrow material-characteristic temperature range and depends upon the cooling rate and the property being measured. When a glass is heated, density fluctuations also dynamically unfreeze over a narrow temperature range, and the volume and specific heat C_p , measured on the heating path differ from those measured on the cooling path [2–5]. Occurrence of such hysteresis loops indicates that the process is not quasithermodynamic; instead, it involves spontaneous relaxation. The resulting irreversibility of liquid-glass transition is found to have little consequence for the entropy values estimated from the $C_p d \ln T$ integral obtained on the cooling and heating paths [3,5–13].

Ergodenhypothese, a concept attributed to Boltzmann who described it in his papers on the kinetic theory of gases [14–18], has been used also for condensed disordered systems, including spin glasses. It postulates that all microstates in phase space corresponding to the surface of constant energy can be, and are, accessed over a sufficiently long period of time. Accordingly, a system is defined as ergodic if the time average of its every measurable property gives the same result as the ensemble average and is defined as nonergodic if it does not. No time scale is specified nor is any intermediate system state defined. In thermodynamic terms, a system is seen as ergodic if its structure fluctuates, with equal probability, through all possible microstates consistent with a macrostate. For simulating the behavior of a system in the energy landscape paradigm, 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. Palmer [19] considered the case of *discontinuously* broken ergodicity when there are no relaxations with characteristic time close to the duration of the observation time in the context of the potential energy surface [20], and he regarded a liquid as ergodic and glass as nonergodic. In discussing its relevance to the concept of microstates and macrostates, Jäckle [21] stressed that there are two (alternative) formalisms of statistical mechanics for describing a nonergodic system. Both Refs. [19,21] discussed the case of the abnormally high barriers giving rise to the concept of disjointed components of the phase space, but Jäckle [21] also considered the possibility of decrease in the entropy on glass formation and did not find it acceptable.

Kivelson and Reiss argued that entropy may decrease on glass formation [22], a view that had been considered, and had been rejected, repeatedly since 1912 [23–26]. To support it, Mauro and co-workers [27,28] treated glass formation as a process of a continuous breakdown of ergodicity in the picture of multidimensional potential energy surface originally proposed by Goldstein [20] but written in the form of enthalpy landscape. They postulated [27,28] that the number of microstates explored by the system depends upon the observational time t_{obs} . As the temperature is decreased, the system gradually becomes trapped in a subset of the available configurational phase space [27]. Thus, by modifying Palmer's approach [19] and using some of Jäckle's [21] discussion, they [27] simulated the properties of a liquid by assuming that there is a continuous breakdown of ergodicity on glass formation, and the configurational entropy S_{conf} decreases to zero. They ignored the facts (i) that a glass has multiplicity of configurations even when it is formed by cooling a liquid at the same rate to the same temperature, i.e., there is a multiplicity of glass structures formed by cooling a liquid identically, and (ii) that Johari-Goldstein (JG) relaxations occur in an otherwise rigid structure of glass [29]. Their premise [27,28] is taken from Palmer's [19] discussion on the role of the observational time t_{obs} in dynamic freezing, namely, that, as the volume

of the configurational phase space explored by the system is reduced, certain sets of transitions among microscopic configurational states become dynamically frozen over a fixed t_{obs} . When T is decreased while keeping t_{obs} fixed, increasing confinement to subsets of the overall phase space decreases both the ergodicity and S_{conf} . This occurs for a fixed cooling rate $q = -(dT/dt)$, for which t_{obs} becomes fixed. Hence, loss of ergodicity was qualitatively related to loss of S_{conf} , and a quantity termed the extent of ergodicity [27], which we denote as x_{ep} , was simulated (Fig. 16 in Ref. [27]). Its plot against T shows a broad sigmoid-shape decrease from $x_{\text{ep}} = 1$ for liquid to $x_{\text{ep}} \rightarrow 0$ for glass.

A similar increasing confinement to subsets of phase space was presumed to occur also with increasing perturbation frequency ν in a relaxation spectra, where ν was taken as proportional to $1/t_{\text{obs}}$ [28], ergodicity and S_{conf} were presumed to decrease with an increase in ν at a fixed T [28], and the relaxation spectra were taken as proof for the notion that x_{ep} was time dependent in the range $0 < x_{\text{ep}} < 1$. Thus, (i) the known increase in the real component of shear modulus G' in the relaxation spectra, which is illustrated in Fig. 1(a), became proof of a decrease in x_{ep} with a decrease in t_{obs} [27,28], (ii) the G' spectra itself became confirmation of *isothermal* glass transition behavior observed simply by decreasing t_{obs} [28], and it was concluded that $x_{\text{ep}} \rightarrow 0$ in the limits of

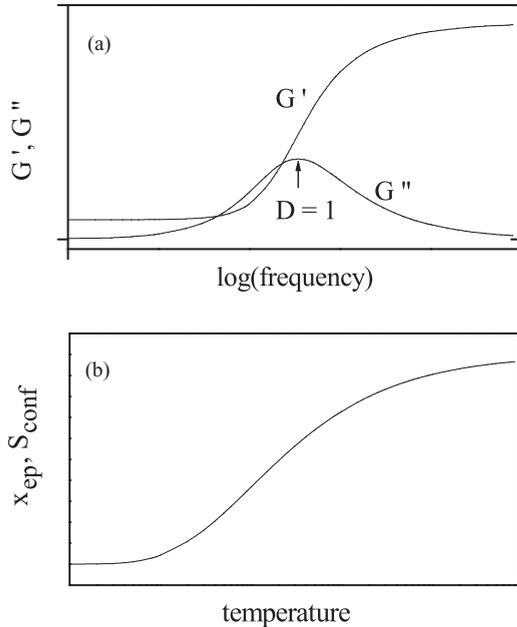


FIG. 1. Illustrations for the dynamic mechanical relaxation: (a) Relaxation spectra of G' and G'' obtained for a distribution parameter $\beta = 0.50$ in the skewed arc distribution. Those who consider ergodic-nonergodic transition in terms of the parameter $D = \tau_0/t_{\text{obs}}$ suggest that the transition occurs when $D = 1$, i.e., at the frequency at which the G'' peak appears. (b) Sigmoid-shape decrease in the ergodicity parameter x_{ep} and S_{conf} to zero values on cooling through the glass formation range. The path is time dependent, and the values differ on heating and cooling. The maximum x_{ep} value is 1 for the ergodic state. In view of the distribution of relaxation times, a liquid is always nonergodic because the slower modes do not come to equilibrium.

$G' \rightarrow G_\infty$ and $t_{\text{obs}} \rightarrow 0$ where G_∞ is the limiting high-frequency shear modulus [28]. The notion of continuously broken ergodicity has been published in several papers since 2007 and has been used for various simulations [27]. Referring to the change in the real component of the specific heat and mechanical relaxation spectra, they finally concluded: “This result serves as experimental and theoretical proof for the nonexistence of residual entropy at absolute zero temperature” [28]. This proof was critically examined in a Comment [30] by pointing out that the specific heat and shear relaxation spectra refer to dynamic susceptibility not loss of S_{conf} . Consequences of the variation in x_{ep} with t_{obs} and T and the role of t_{obs} were not considered in that Comment.

If we accept their interpretation [28] of the G' spectra and the notion that x_{ep} varies between 1 and zero [27], a revision of our understanding of the relaxation phenomenon would be required. Here, we examine if this could be the case and find that features of the mechanical relaxation spectra are *inconsistent* with their proof [28], and the spectra do *not* “. . . confirm this isothermal glass transition behavior for mechanical properties, such as shear modulus” [28]. Moreover, the postulate [27,28] leads to untenable consequences for the properties of liquids and glasses.

II. OBSERVATIONAL TIME, GLASS FORMATION, AND RELAXATION SPECTRA

A liquid *appears* to be rigid if the observational time t_{obs} is exceedingly short, just as an object in continuous random motion appears to be stationary in a short exposure image. Accordingly, the ratio of the characteristic relaxation time τ_0 to t_{obs} has been used for discussing dynamic freezing and loss of ergodicity. Briefly, dynamic freezing occurs when the ratio $D = \tau_0/t_{\text{obs}}$ is equal to 1, where τ_0 is taken as the internal time, equal to the time necessary for structural rearrangement, and t_{obs} is taken as the external time of an experiment [28]. When a liquid is cooled at a fixed rate $q = -(dT/dt)$, t_{obs} becomes fixed, and τ_0 rapidly increases from $\tau_0 \ll t_{\text{obs}}$ ($D < 1$) to $\tau_0 > t_{\text{obs}}$ ($D > 1$), and the liquid is said to dynamically be frozen when $D > 1$. The temperature at which $D = 1$, is the fictive temperature T_f , which is high when q is high and is low when q is low. If one chooses the temperature at which $\tau_0 = 1$ ks (viscosity of $\sim 10^{13}$ Poise) as T_g , and keeps the sample at T_g , the state is said to behave as glass when $t_{\text{obs}} < 1$ ks ($D > 1$) and behave as a liquid when $t_{\text{obs}} > 1$ ks ($D < 1$). When kept at a fixed $T < T_g$, the glass structure spontaneously relaxes to a lower energy structure and, as t_{obs} increases, T_f decreases toward the fixed T of glass, and τ_0 increases asymptotically [1,29,31]. Thus, D , which was initially higher than 1, decreases to a value below 1.

The quantity D was originally suggested for expressing the deformation of glass by viscous flow over a very long time period; D , which is initially much greater than 1, decreases to zero as $t_{\text{obs}} \rightarrow \infty$. We point out that D is a decreasing function of t_{obs} also in a step-response experiment as expressed by the Maxwell-Voigt models [32]: When a sample is kept under a fixed strain γ_0 and the stress σ is measured with $t_{\text{obs,SR}}$, the time from the beginning of the relaxation response [29,32], one determines $G(t_{\text{obs,SR}}) = \sigma(t_{\text{obs,SR}})/\gamma_0$. The plot of $G(t_{\text{obs,SR}})$ against $\ln(t_{\text{obs,SR}})$ shows that G_∞ decreases to G_0 according to

an inverted sigmoid-shape curve [32], and $D \rightarrow 0$ in the limit $t_{\text{obs,SR}} \rightarrow \infty$.

When a spectral frequency ω (rad/s) is taken as equal to $1/t_{\text{obs}}$, the quantity t_{obs} is taken to correspond to the period of one sinusoidal cycle. In a relaxation spectrum, therefore, $D = \omega_m \tau_0$, where ω_m is the frequency (in rad/s) at which the peak in the imaginary or loss component G'' of the complex shear modulus $G^* = G' + iG''$ appears [29,32]. Thus, when the loss of mechanical energy is maximum, $\tau_0 = 1/\omega_m$, and $D = 1$. In the spectra of G' and G'' illustrated in Fig. 1(a), the state is seen as dynamically *unfrozen*, at internal equilibrium or ergodic, for time scales of $\omega < \omega_m$ and is seen as dynamically *frozen*, out of equilibrium or nonergodic for the time scales of $\omega > \omega_m$. Ergodic-nonergodic transition is seen to occur at ω_m . The state is glass for time scales shorter than 1 ks ($\omega_m > 1$ mrad/s). When $t_{\text{obs,SR}}$ is taken as equal to $1/\omega$, $G'(\omega)$ differs from $G(t_{\text{obs,SR}})$, and this distinction needs to be maintained. Both $G'(\omega)$ and $G(t_{\text{obs,SR}})$ approach the relaxed value G_0 in the upper limit of $t_{\text{obs,SR}} = 1/\omega$ and approach the unrelaxed value G_∞ in the lower limit of $t_{\text{obs,SR}} = 1/\omega$.

It is known that a relaxation process in ultraviscous liquids has a broad distribution of relaxation times [29,32], i.e., a relaxation spectrum may be represented by a superposition of a multiplicity of spectra, each with a single relaxation time, formally from near zero to an uppermost value, depending upon the model used. Accordingly, not all transitions among microscopic configurational states would occur in a liquid; some transitions would always remain dynamically frozen even at high T . In this sense, a liquid should be regarded as nonergodic, unless, as in Boltzmann's *ergodenhypothese*, $\omega \rightarrow 0$ or $t_{\text{obs}} \rightarrow \infty$. We stress that Palmer (Sec. 2.1, Ref. [19]) recognized its significance when he used Feynman's words that, in thermal equilibrium all the fast things have happened and all the slow things have not, and then suggested that equilibrium depends crucially on t_{obs} , which itself determines the meaning of fast and slow. Thus, different values of t_{obs} give different equilibria. We point out that, as the distribution of relaxation time increases with decreasing T , the shape of x_{ep} against $t_{\text{obs}} (=1/\omega)$ for an apparently ergodic liquid would change.

In a recent monograph on relaxation and diffusion phenomenon [29], Ngai describes how data obtained from various relaxation spectroscopy techniques are interpreted in the study of the molecular dynamics of liquids and glasses. (Elements of relaxation spectroscopy appear in most undergraduate textbooks.) Briefly, the dynamics of molecular motions that produce density fluctuations are observed by perturbing a state from its equilibrium. It is also worth stressing that biasing of density fluctuations by a perturbation does not have the same consequences as dynamic freezing of density fluctuations on the time scale of ω , and therefore, a relaxation process is not the same as dynamic freezing over a certain t_{obs} for which D is used. Therefore, the relaxation spectra would not indicate D nor would they indicate the implied nonergodicity or entropy loss. For that reason, we maintain that G' and G'' spectra are distinct from the G' - ω , and G'' - ω plots. To elaborate, (i) G^* is consistent with the fluctuation-dissipation theorem, the spectra obey the Kramers-Kronig relations and are analyzed to obtain τ_0 , the distribution parameter β , and the relaxed and unrelaxed values of the shear moduli [29,32] G_0 and

G_∞ . In contrast, the G' - ω and G'' - ω plots do not have these attributes. (ii) A relaxation spectrum is a Fourier transform of a step-function response described by the Maxwell-Voigt elements [29,32], i.e., linear combinations of springs and dashpots, and the spectra of G' and G'' on the positive side of the ω cycle are identical to those on the negative side. If a Fourier transform could be obtained for the G' - ω and G'' - ω plots, the values on the two sides would be different.

Maggi *et al.* [33] published a detailed study of the G' spectra of the α -relaxation process in a variety of liquids covering a frequency range of 10 mHz–10 kHz. They interpreted it in terms of dynamic susceptibility in which G' continuously increases with increasing ω and G'' spectra show peaks when $\omega = \omega_m$; both features are a consequence of a phase lag between the oscillating response and the stimulus. Since G' increases only when $G'' > 0$, there is a loss of energy in perturbing the density fluctuations. They [33] used the data to investigate the dynamics of the α -relaxation process and occurrence of the JG relaxation in ultraviscous liquids [29] and did not interpret the increase in G' and the concomitant peak in G'' as a process of freezing or unfreezing of density fluctuations or as a process of isothermal glass transition. Surprisingly, Mauro *et al.* [28] used the G' feature of the spectra in the studies of Maggi *et al.* [33] (and of such α -relaxation spectra in general) to assert [28]: "Further experiments, such as the shear-mechanical spectroscopy work of Maggi *et al.* [33] confirm this isothermal glass transition behavior for mechanical properties, such as shear modulus." Because of the difference in the consequences of molecular relaxation and dynamic freezing, this assertion is unjustifiable.

III. MECHANICAL RELAXATION AND BRILLOUIN LIGHT SCATTERING

In addition to G , one measures the compressibility modulus K , the longitudinal modulus $M = K + (4/3)G$, and the velocity of propagation of ultrasonic waves $u = (M/\rho)^{1/2}$ in their respective ω ranges from millihertz to gigahertz by using techniques of torsional oscillations [29,32–35], linear vibrations, propagation of ultrasonic waves [36–43], and Brillouin light scattering (BLS) [43–52]. The majority of such studies yield isochrones of G , K , M , and u and attenuation of propagating ultrasound. Alig [41] and Fluodas *et al.* [43] discussed the features of BLS, ultrasonic, dielectric, and specific heat relaxations and showed that they yield the same information about molecular dynamics of a liquid.

BLS is used to study dynamics of density fluctuations on a time scale of 10–100 ps at high temperatures. Depending upon the wave vector propagating in the medium, it probes relaxation that is associated with the dissipation of the phonon energy in the structure. Since one determines the propagation and damping of acoustic modes at gigahertz frequencies, BLS methods have become specially useful for (a) investigating the density fluctuations that show up as features of the α relaxation in the G^* and M^* at T far above T_g where T_g is the temperature at which dynamic freezing occurs on the (laboratory) time scale of the BLS experiments [42–52], and (b) for detailed investigations of G_∞ , M_∞ , K_∞ , and u_∞ . The state remains at internal equilibrium over a broad temperature range between the G'' and the M'' peaks and T_g , a range over which $\omega\tau_0 \gg 1$,

$G' \rightarrow G_\infty$, and $M' \rightarrow M_\infty$. We use the available results from the BLS studies to determine whether the ergodicity and entropy could continuously decrease as τ_0 increases on cooling toward T_g .

Kieffer and co-workers [44–47] have performed comprehensive BLS studies of binary oxide melts and glasses. We digitized their plots [44–47] to obtain the M' and M'' data and constructed the isochrones given here as an example of the general features in Fig. 2 where T_g is marked for one plot. In the temperature range $T > T_g$, the M' and M'' values (plotted on the same scale of the ordinate) for several B_2O_3 - K_2O compositions [44] and for TeO_2 -20 mol % K_2O [45] change reversibly with changes in T , and M'' shows the characteristic α -relaxation peak at a temperature T_{peak} where $D = 1$. The increase in M' observed on cooling to T below T_{peak} in Fig. 2, as generally observed in the studies of Kieffer and co-workers [41–47], is partly due to an additional relaxation process in

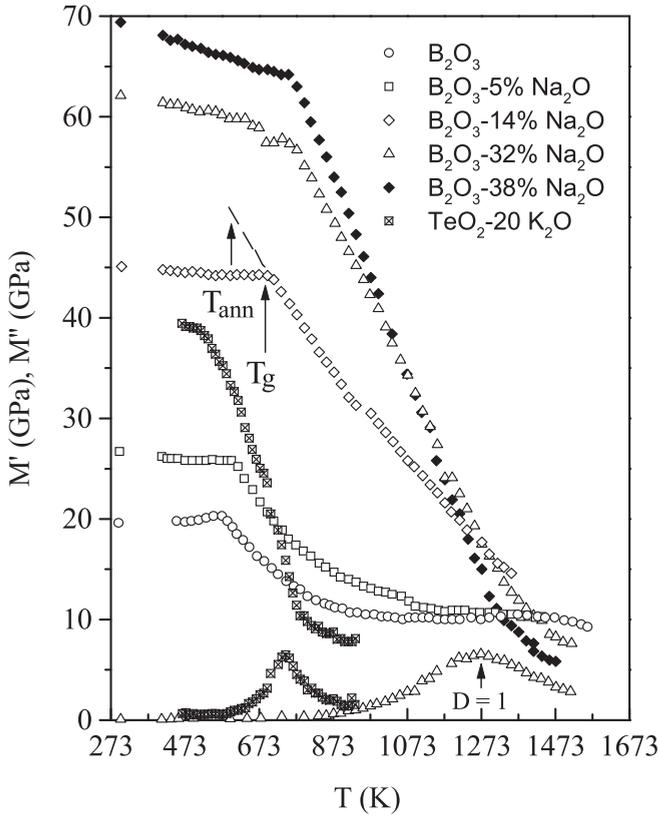


FIG. 2. Plots of the real and imaginary components of M^* of several compositions in their liquid and glassy states measured with BLS by Masnik *et al.* [44] and Kieffer *et al.* [45]. A change in the slope of the M' plot occurs in the liquid-glass transition at temperature T_g on the time scale of measurements, which is usually defined as ergodic-nonergodic transition. M' and M'' (on the same scale of the ordinate) observed at $T > T_g$ are reversible and are due to the α -relaxation process and, at $T < T_g$, are irreversible. M'' shows a peak at a temperature at which τ_0 of the melt is equal to the reciprocal of the frequency (in rad/s) in the gigahertz range, i.e., $D = 1$ at this peak. The sigmoid-shape plot of M' is compromised beyond recognition by the broadness of the M'' plot for the borate compositions. It is barely evident for the TeO_2 -20 mol % K_2O [45]. T_{ann} is the annealing temperature at which the state relaxes and M' of glass increases to M_∞ of the liquid.

the liquid state [46] and is partly due to an increase in the distribution of the relaxation time (broadening of the relaxation spectra), which seems more for the B_2O_3 - K_2O compositions than for the TeO_2 -20 mol % K_2O . (It has been found that M' for several liquids [45–47] does approach a plateau-like value on cooling to T below T_{peak} , but the data for their glasses do not extend low enough below T_g , and, therefore, are not shown here.) M' is close to M_∞ for $\omega\tau_0 \gg 1$ and is close to M_0 for $\omega\tau_0 \ll 1$. In general, the slope for the M_∞ isochrone, as in Fig. 2, is greater than that for the M_0 isochrone, including polymers, such as poly(phenyl-methyl siloxane) studied at 1-MHz frequency [41], and M_∞ at $T > T_g$ does not change with time as for molecular liquids and polymers [43,48–53]. On further cooling, the α -relaxation process becomes dynamically frozen at T_g to the glassy state, and the slope of the M' (or M_∞) plot against T decreases (Fig. 2) as the glass forms. The G'' and M'' values for both glass and ultraviscous liquid at the same temperatures are close to zero. In Fig. 2, the decrease in the slope at T_g is analogous to the decrease observed in the slopes of the density and the refractive index plots against T . It shows that dM_∞/dT contains the effects of changes in both the density and the number of available configurations, but dM'/dT of glass contains only the effect of the changes in the density, i.e., the part due to configurational changes becomes dynamically frozen at $T < T_g$. In general, the M' and G' of glass increase with time toward the M_∞ and G_∞ of the liquid extrapolated to $T < T_g$ [36,40,42] as indicated for M' in Fig. 2. Atomic and other types of glasses have shown a similar decrease in the slope at their T_g 's and a similar increase in M' and G' values with time on annealing [54–58].

IV. NOTIONS OF ERGODICITY AND ENTROPY AND RELAXATION SPECTRA

In simulations, the parameter x_{ep} [27] and S_{conf} [59] were shown to decrease to zero when a liquid, on cooling, formed a glass. The decrease occurred in a sigmoid-shape manner over an exceptionally broad temperature range, as illustrated in Fig. 1(b). A similar sigmoid shape, but an increase, in G' occurs with an increase in the spectral frequency [Fig. 1(a)] or with a decrease in t_{obs} ($=1/\omega$). Both the decrease in x_{ep} [27] and S_{conf} [59], on cooling, and an increase in G' with a decrease in $1/\omega$ were interpreted as a consequence of increasing confinement to subsets of phase space and were used, thus, to support the view that entropy is lost on the time scale of spectral frequency and G' serves as the confirmation of isothermal glass transition [28].

To investigate it, first, we recall that, for each dispersion spectrum, there is a unique loss and $\tan \delta$ spectra,

$$\frac{M' - M_0}{M_\infty - M_0} = \omega \int_0^\infty \sin \omega t g(t) dt, \quad (1)$$

and

$$\frac{M''}{M_\infty - M_0} = \omega \int_0^\infty \cos \omega t g(t) dt, \quad (2)$$

In general, $g(t) \equiv C(t)/\langle |\rho_q(0)|^2 \rangle$ where $\langle |\rho_q(0)|^2 \rangle$ denotes the mean square density fluctuations, $C(q,t)$ is the density time autocorrelation function at wave number q , and $g(t) = \exp[-(t/\tau)^\beta]$ [29,43]. Were the spectra to indicate dynamic

freezing of density fluctuations on the time scale of ω and if both $x_{\text{ep}} \rightarrow 0$ and $S_{\text{conf}} \rightarrow 0$ in the limit $\omega \rightarrow \infty$ ($t_{\text{obs}} \rightarrow 0$), the relaxation functions would be *unusable* for obtaining the dynamics of molecular relaxation in terms of τ_0 and β .

Second, if x_{ep} and S_{conf} were to decrease on decreasing t_{obs} (increasing ω) [28], the configurational part of free energy $G_{\text{conf}} (=H_{\text{conf}} - TS_{\text{conf}})$ would increase, and the net free energy ($=G_{\text{conf}} + G_{\text{vib}}$ where G_{vib} refers to the vibrational part) would reach its maximum value as $S \rightarrow 0$ in the limit $t_{\text{obs}} \rightarrow 0$. Therefore, G_{conf} would reversibly change between its values of $(H_{\text{conf}} - TS_{\text{conf}})$ at the lowest ω and of H_{conf} at the highest ω according to the shape of the plots of x_{ep} and S_{conf} against ω . Since the increase in solubility, vapor pressure, and chemical reactivity of a glass over the crystal phase are proportional to the exponential of free energy divided by RT , an ω -dependent G_{conf} would mean that the magnitude of these properties at a fixed T would depend upon t_{obs} . A material would be expected to be greatly more soluble, vaporizable, and reactive when observed for a short time and less so when observed for a long time, reaching its highest value in the limit $t_{\text{obs}} \rightarrow 0$ or $\omega \rightarrow \infty$. We found no studies indicating that these properties increase with decreasing t_{obs} . Therefore, modification of the Gibbs entropy formula to accommodate the notion that entropy depends upon spectral ω (or t_{obs}) is unnecessary.

Third, ω -dependent S_{conf} in a spectrum is not the same as t_{obs} -dependent S_{conf} , because there is loss of energy at a spectral frequency, which is given by $\Delta W = \pi \gamma_0^2 G''$ per cycle of frequency where γ_0 is the perturbation strain amplitude [32] and there is no such loss in determining S_{conf} as a function of t_{obs} in simulation. Moreover, x_{ep} and S_{conf} are not treatable as dynamic susceptibilities with real and imaginary components. If x_{ep} , S_{conf} , and G_{conf} were to have their unique values corresponding to G' , the plots of x_{ep} , S_{conf} , and G_{conf} against ω would show time-temperature superposition similar to that observed for the normalized spectra of G' [29,32,35,39]. But such a superposition is not known for thermodynamic functions.

Last, the notion of ω -dependent x_{ep} and S_{conf} is inconsistent with the Adam-Gibbs relation of viscosity to S_{conf} , $\eta = \eta_0 \exp(C/TS_{\text{conf}})$ [60] where η_0 and C are constants and η is directly proportional to τ_0 . The reason is that any decrease in S_{conf} with increasing ω would imply that equilibrium values of η and τ_0 vary with ω . A state does not switch between more ergodic and less ergodic by changing ω . That one *observes* less and less, and ultimately nothing of an occurrence as $t_{\text{obs}} \rightarrow 0$ or $\tau_0 \rightarrow \infty$, is obvious without resorting to a postulate of continuous reduction in the configurational phase space explored by the system or ergodicity. Dyre [61] pointed out that glass formation has little in common with ergodic-nonergodic transitions of various lattice models, the ideal mode-coupling theory, or with the jamming transitions of granular media; Schmelzer and Gutzow [62] and Gujrati [63] provided arguments against it for glass transition, and Goldstein [11,12,64] argued that the time period required to explore all configurations is astronomically long, and he further showed that the notion of loss of S_{conf} on glass formation violates the second law of thermodynamics and allows the possibility of a perpetual motion machine of the second kind.

There is a difference between the relaxation phenomenon [29,32] and the postulate that increasing confinement to subsets of the overall phase space would increase G' or M' because of continuous decreases in ergodicity and S_{conf} [27,28]. As discussed earlier here, the α -relaxation process is consistent with the fluctuation-dissipation theorem, and its spectra obey the Kramers-Kronig relation. Although perturbations in the spectral condition $\omega\tau_0 \gg 1$ do probe the out-of-phase response of the already occurring density fluctuation modes and some of the energy used in perturbation is absorbed by the liquid whose temperature rises, it does *not* mean that some density fluctuation modes do not occur when ω is high. From the standpoint of thermodynamics, all these modes contribute to S_{conf} at all frequencies.

The G' and M' isochrones show the α -relaxation process and not a reversible loss and regain of ergodicity or S_{conf} . As the G_∞ and M_∞ values seen in an isochrone of a liquid contain a configurational contribution, S_{conf} of the liquid is finite. According to the notion of ω -dependent ergodicity [28], dynamics freezing would have already occurred on the scale of $t_{\text{obs}} (=1/\omega)$, and both G_∞ and M_∞ values would correspond to an almost zero value of x_{ep} and of S_{conf} . At a temperature significantly above T_g , $D (= \omega\tau_0)$ is about 10^{10} for gigahertz frequencies when τ_0 of 1 s. (In contrast, $D = 1$ at the M'' peak in Fig. 2.) In Palmer's [19] view, ergodicity would be broken at the temperature at which the slope of the plots in Fig. 2 decreases, i.e., when density fluctuations freeze on cooling through T_g .

We conclude that the postulate of increasing confinement to subsets of the overall phase space is not supported by increasing G' found either in the relaxation spectra or in an isochrone. Moreover, if $G(t_{\text{obs,SR}}) [= \sigma(t_{\text{obs,SR}})/\gamma_0]$ is measured in step-response experiments performed at different temperatures and the G value for a fixed $t_{\text{obs,SR}}$ interpolated from the data is plotted against T , the plot would have a negative slope. The slope would be less at $T < T_g$ than at $T > T_g$, resembling the change observed in the corresponding plots of the density and refractive index. The change in slope would not indicate, as explained here earlier, loss of S_{conf} .

Since we find no proof of t_{obs} , or ω -dependent S_{conf} , nor of isothermal glass transition, we inquire how these notions [28] came about. It seems that the increase in G' , the postulated loss of S_{conf} , the failure of a system to reach equilibrium, and the time and temperature dependences of all were regarded as manifestations of loss of ergodicity. These were then linked, (i) to the hypothesis that the state of a system was trapped in a specific description of configurational minimum in the simple (one-dimensional) enthalpy landscape by using a set of conditional probabilities, (ii) to an interpretation of ergodicity out of several already known, and (iii) to the view that $t_{\text{obs}} = 1/\omega$ in $D = \tau_0/t_{\text{obs}}$, which was not the original definition of D . All was performed by ignoring the energy loss indicated by the G'' peak. We find that such a framework is too fragile to either support the Kivelson-Reiss [22] view of zero residual entropy or to require that theories of the relaxation spectra be reconsidered.

V. CONCLUSION

Features of the mechanical relaxation spectra of a liquid are determined by the density relaxation function and not by the

dynamic freezing of configurational degrees of freedom or by a decrease in the time-dependent fractional ergodicity. Were there a loss of frequency-dependent entropy due to dynamic freezing, the solubility, vapor pressure, and chemical reactivity would be extremely high when observed for a short time and would be low when observed for a long time, and all would change by a large amount on annealing a glass. There have been no such indications.

Relaxation spectra include the imaginary component of dynamic susceptibility, which yields the ω -dependent loss of energy, and there is a difference between t_{obs} and $1/\omega$. These need to be taken into account in relating the spectra to the entropy and ergodicity loss. We found no support for the postulate that an increase in G' with spectral frequency

is evidence of a decrease in fractional ergodicity and entropy [28]. The notion that both $x_{\text{ep}} \rightarrow 0$ and $S_{\text{conf}} \rightarrow 0$ as $G' \rightarrow G_{\infty}$, in the limit $\omega \rightarrow \infty$, seems to have no basis.

If we accept the definition of ergodicity based upon the observational time, liquids would always be nonergodic because not all molecular degrees of freedom in their structure come to equilibrium within a finite time. Not only does this cause doubts about using the ergodic-nonergodic transition for glass formation, but also puts into question the use of the second law in the Gibbs free energy relation for liquids. The Maxwell-Voigt models for step response used for viscoelastic spectra are uncommutable to the path-irreversible thermodynamics that characterizes glass transition.

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