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Signature of ergodicity in the dynamic response of amorphous systems

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We have analyzed dynamical measurements from materials near their liquid-glass transition. The primary response is accurately characterized by a model for dispersive excitations on specific distributions of independently relaxing domains. Liquids have an equilibrium (Gaussian) distribution of domain sizes, which changes abruptly to a locally random (Poisson-like) distribution in the glass. When quenched to a temperature initially in the glass phase, after a definite anneal time, the Poisson-like distribution changes abruptly back to the Gaussian distribution characteristic of a liquid.

Although vitrification is usually manifested by smooth changes in dynamic response, researchers have long searched for the possibility of an underlying glass transition.[1,2] The change from liquidlike to glasslike behavior occurs over a range of temperatures near the glass transformation temperature T_g, but a true transition (as defined by an abrupt change in an order parameter) must occur sharply at a critical temperature. The order parameter most often associated with the glass transition is related to the change in ergodicity between the (equilibrium) liquid and the (nonergodic) glass. High-frequency measurements[3,4] show nonequilibrium behavior at temperatures well above T_g, but these deviations depend on the time scale of the measurement, consistent with smooth convergence toward T_g at lower frequencies. We have carefully examined dynamic response data from several amorphous materials in the vicinity of T_g. We find a subtle, but significant, distinction between the response of ergodic and nonergodic phases. The temperature at which a substance becomes nonergodic (T_e) depends on the cooling rate, or equivalently on the anneal time (t_A) at constant temperature, but not on the time scale of the measurement, thus providing clear experimental evidence for a dynamical transition at $T_e(t_A)$.

Since 1854, the Kohlrausch-Williams-Watts[5,6] (KWW) stretched exponential, $P(t) \propto e^{-(t/\tau)^\beta}$, has been used to characterize the dynamic response of a wide variety of amorphous materials. The KWW function is a simple mathematical expression that gives generally good agreement with many different measurements.[7] Unfortunately, this empirical expression is also a common approximation to many different models.[8,9] Furthermore, the stretched exponential has divergent slope at short times, and hence it can only be an approximation valid over a limited dynamic range; indeed, measurements over sufficient range invariably demonstrate deviations from the KWW function. Distinguishing a liquid from a glass requires a more sophisticated analysis. We use a specific physical model for nonexponential relaxation. The model has been shown to provide a more accurate description for the observed response from dozens of different materials including magnetic relaxation in spin glasses[10] and ferromagnets,[11] stress relaxation in glasses,[12,13] and dielectric susceptibility of glass-forming liquids.[14,15] Here, we utilize this model to identify ergodicity and clarify the differences between liquids and glasses.

The model is based on the assumption that a macroscopic sample contains a heterogeneous distribution of dynamically correlated domains. We define a dynamically correlated domain as a region where dispersive excitations (phonons, polaritons, etc.) relax with a single (locally uniform) relaxation rate. Quantum mechanically, a domain may correspond to a region where particles form a single (coherent) many-bodied system, thus ensuring uniform relaxation throughout the domain. Thermodynamically, a domain is a canonical system, which, during relaxation, need not be in equilibrium with neighboring domains or the thermal bath. Four-dimensional NMR has shown that the nonexponential relaxation in a glass-forming liquid is due to spatially heterogeneous, dynamically correlated domains.[16] Assuming a domain-size distribution n_s, with size-dependent initial response P_s and relaxation rate w_s, the net relaxation is the weighted sum over all sizes $P(t)=\sum_{s=0}^{\infty}[P_s n_s]\exp(-t w_s)$. Some physically reasonable assumptions are made to obtain the size dependences of P_s, n_s, and w_s.

The initial response per particle is assumed to be homogeneous, so that $P_s \propto s$. The relaxation rate is assumed to obey activated (Arrhenius-like) behavior $w_s \propto e^{-\delta E_s/k_B T}$. The excitation density of states is assumed to be proportional to the volume (size) of a domain, so that the energy-level spacing is $\delta E_s = \pm\Delta/s$, where Δ is related to an energy bandwidth. It is convenient to define a dimensionless energy ratio $\varepsilon = \pm\Delta/k_B T$, so that the relaxation rate becomes $w_s \propto e^{-\varepsilon/s}$. Finally, some randomness is assumed to obtain one of two specific domain-size distributions.

Assuming quenched (local) randomness, there is random probability (p) that a given particle is dynamically correlated with one of its neighbors. Percolation theory[17] predicts that for p less than the critical concentration for bond percolation (p_c) there are only finite domains of correlated particles, whereas for $p > p_c$ there is an infinite backbone in addition to finite domains. Percolation theory also provides specific predictions for the distribution of finite domains. For $p > p_c$ in three dimensions, the probability of finding a domain of size s is the Poisson-like distribution[18–20] $n_s \propto s^{-\theta} e^{-(C's)^{\zeta}}$, where $C' \propto |p - p_c|^{1/\sigma}$ with $\sigma = 0.45$, and the size-scaling exponents are $-\theta = \frac{1}{9}$ and $\zeta = \frac{2}{3}$. Using $x = C's$, the net relaxation of a locally random system is

$$P(t) = P_i \int_0^{\infty} [x^{10/9} e^{-x^{2/3}}] \exp(-t w_{\infty} e^{-C/x}) dx \ . \tag{1}$$

Here P_i is proportional to the initial response, w_{∞} (which is related to an attempt frequency) determines the time scale of the relaxation, and the "correlation coefficient" $C = C'\varepsilon$ governs the width and entire shape of the response. For weakly interacting particles $\Delta \ll k_B T$, or near percolation threshold $C' \approx 0$, the correlation coefficient is small, and Eq. (1) reduces to single relaxation-rate (Debye-like) behavior, whereas for $|C| \gg 1$ the effective distribution of relaxation times is extremely broad.

Assuming equilibrium (long-ranged) randomness, with deviation σ about an average domain size $\bar{s}$, the appropriate distribution is Gaussian $n_s \propto e^{-[(s-\bar{s})/\sigma]^2}$. Using $x = s/\sigma$, the net relaxation of an ergodic system becomes

$$P(t) = P_i \int_0^{\infty} [x e^{-(x-\bar{x})^2}] \exp(-t w_{\infty} e^{-C/x}) dx \ . \tag{2}$$

Here the correlation coefficient is $C = \varepsilon/\sigma$, and the additional adjustable parameter $\bar{x} = \bar{s}/\sigma$ is the (scaled) average domain size. In principle, $\bar{x}$ could accommodate additional variations in the shape of the response, but (within experimental resolution) for every ergodic system we have examined the ratio $\bar{x}/|C| = \bar{s}/|\varepsilon|$ is constant, independent of temperature. Furthermore, this constant $\bar{s}/|\varepsilon| = \bar{s}/(\Delta/k_B T) = 0.19 \pm 0.02$ from stress relaxation and dielectric susceptibility of glass-forming liquids, is similar to that obtained from magnetic relaxation in single crystals of iron, $\bar{s}/|\varepsilon| = 0.21 \pm 0.02$.[21] This suggests that $\bar{s}/\Delta$ is inversely proportional to temperature over at least two orders of magnitude in temperature, *and,* at a given temperature, $\bar{s}/\Delta$ is identical for phonons and polaritons in glass-forming liquids, as well as for magnons in crystalline iron. This remarkable pervasiveness may account for the common dynamic scaling found in several glass-forming liquids.[14] Experimentally, Eq. (2) with $\bar{x} = 0.20|C|$ provides excellent fits to a wide variety of data with the width and entire shape of the response again governed by a single adjustable parameter. Other systems, however, require different values of $\bar{x}/|C|$. For example, stress relaxation in high-density polyethylene and polycrystalline cadmium[22] have $\bar{x}/|C| = 0.045 \pm 0.005$, which may explain the additional parameter necessary to characterize the dynamic scaling in other materials.[23]

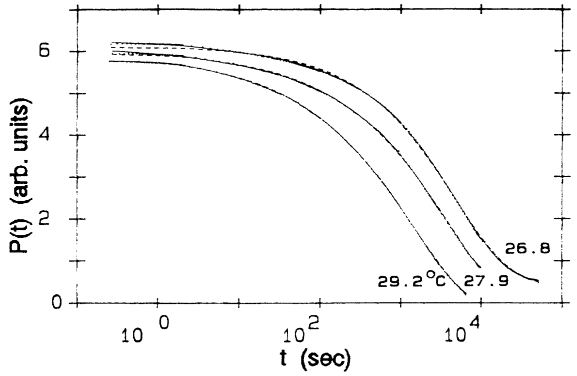

FIG. 1. Stress relaxation in $60\text{AgI-}35\text{Ag}_2\text{SO}_4\text{-}5\text{Ag}_2\text{WO}_4$ at three temperatures below $T_e = 29.9\,^{\circ}\text{C}$ (Ref. 12). The best fits to Eq. (1) (solid curves) and the KWW function (dashed curves) are shown for comparison.

Stress-relaxation measurements[12] on the ionic glass $\text{AgI-Ag}_2\text{SO}_4\text{-Ag}_2\text{WO}_4$ are shown in Fig. 1. Measurements were made by quenching the sample from above $T_g \approx 33\,^{\circ}\text{C}$, stabilizing at the measurement temperature for $t_A \approx 15$ min, then measuring the time-dependent stress at constant strain. Best fits using the KWW function (dashed curves) show significant deviation at short times. Equation (1), with the same number of adjustable parameters, shows excellent agreement throughout the range of data (solid curves). Indeed, Table I shows that the average χ^2 deviation using Eq. (1) (χ_1^2) is significantly smaller than that using the KWW function (χ_β^2). Furthermore, despite the additional adjustable parameter in Eq. (2), Eq. (1) gives better fits to these data. Below $T_e = 29.9 \pm 0.6\,^{\circ}\text{C}$, even after stabilizing for 15 min, the dynamic correlations retain local randomness. Above T_e, the Gaussian distribution with $\bar{s}/|\varepsilon| = 0.20$ yields the smallest χ^2 deviations; see Table I.

The frequency-dependent dielectric susceptibility is the

TABLE I. Statistical comparison of χ^2 deviations from fits to the dynamic response in some amorphous systems. Negative values of $\ln\chi_1^2/\chi_\beta^2$ indicate Eq. (1) fits better than the KWW function, of $\ln\chi_1^2/\chi_2^2$ indicate Eq. (1) fits better than Eq. (2), and of $\log\chi_3^2/\chi_\beta^2$ indicate Eq. (2) or (3) with $\bar{x} = 0.20|C|$ fits better than the KWW function.

	Glass $T < T_e$		Liquid $T > T_e$
System	$\ln\chi_1^2/\chi_\beta^2$	$\ln\chi_1^2/\chi_2^2$	$\ln\chi_3^2/\chi_\beta^2$
$\text{AgI-Ag}_2\text{SO}_4\text{-Ag}_2\text{WO}_4$	-0.686 ± 0.004	-0.06 ± 0.08	-0.12 ± 0.06
AgI-AgPO_3	-0.22 ± 0.03	-0.05 ± 0.01	$+0.2 \pm 0.2$
Phenolphthalein	-0.435 ± 0.011	-0.05 ± 0.02	-0.09 ± 0.03
Salol			-0.037 ± 0.013

Fourier transform of $-d[P(t)]/dt$. From Eq. (2),

$$\chi(\omega)=P_i\int_0^{\infty}[xe^{-(x-\bar{x})^2}]\frac{1+i(\omega/w_x)}{1+(\omega/w_x)^2}dx\ , \tag{3}$$

where $w_x=w_{\infty}e^{-C/x}$. We have analyzed the dielectric absorption (χ'') of liquid salol[14] using Eq. (3) and the frequency-dependent forms of Eq. (1) and the KWW function. Table I shows that Eq. (3) with $\bar{x}/|C|=0.20$ gives superior agreement with the data. Such naive statistical comparison, however, is not necessarily the best way to demonstrate the viability of the model. The KWW function is an accurate approximation to Eqs. (1), (2), or (3) at frequencies (or times) that include the maximum response regime, where the most interesting and reliable data are usually obtained. Significant deviations appear at higher frequencies (shorter times), where they make only minor contributions to the net χ^2 deviation. Figure 2 is a log-log plot of χ'' from salol at 219 K. In the vicinity of the peak, the KWW function (dotted line) gives good agreement with the data. Clear deviations from KWW behavior do not begin until about three orders of magnitude above the peak frequency, where χ'' is less than one-tenth its peak value. Although the net magnitude of deviation is small, this log-log plot emphasizes the unequivocal departure from KWW behavior. Equation (3) with $\bar{x}/|C|=0.20$ (solid curve) shows excellent agreement over more than 13 orders of magnitude in frequency. The frequency-dependent form of Eq. (1) (dashed curve) shows subtle, but significant, deviation between this liquid and the nonequilibrium response expected from an otherwise identical glass.

With decreasing temperature, stress relaxation in AgI-Ag_2SO_4-Ag_2WO_4 exhibits a smooth broadening of the response, with no obvious discontinuity in the shape of the relaxation between 30.5 and 29.2 °C (Fig. 3). However, analysis using the Gaussian distribution of domains reveals a sharp change between these two temperatures. The inset of Fig. 3 shows the temperature dependence of the ratio of two adjustable parameters $\bar{x}/|C|$, from fits to dielectric susceptibility in salol using Eq. (3), and stress relaxation in phenolphthalein and AgI-Ag_2SO_4-Ag_2WO_4 using Eq. (2). Above the ergodicity temperature, within experimental resolution, $\bar{x}/|C|=0.20$ for all temperatures, materials, and measurement techniques. At T_e, $\bar{x}/|C|$ drops sharply toward zero. Below T_e, analysis of data using Eq. (2) yields physically unreasonable average domain sizes ($\bar{x}\lesssim 0$) as the Gaussian distribution attempts to mimic the Poisson-like distribution. Indeed, Table I shows that Eq. (1) (with one fewer adjustable parameters) provides better fits to these data. Although $\bar{x}/|C|$ drops by nearly three orders of magnitude from 30.5 to 29.2 °C, indicating a discontinuous (first-order) dynamical transition from ergodic (Gaussian) to nonergodic (Poisson-like) distributions of domains, integration over domain sizes obscures the change in net response. Regardless of interpretation, ergodicity may be identified by using Eq. (2) as an empirical expression, without resorting to any specific model.

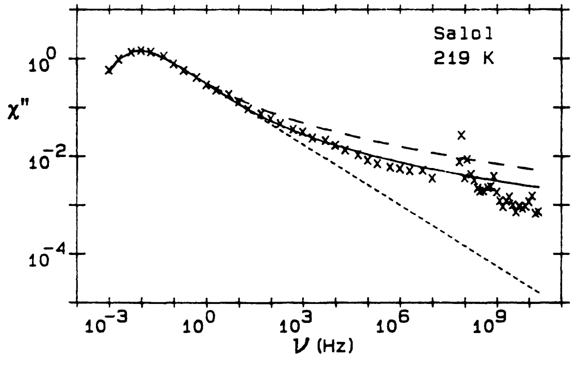

FIG. 2. Dielectric absorption in salol as a function of frequency at 219 K (Ref. 14). Agreement with Eq. (3) (using $\bar{x}=0.20|C|$, solid curve) indicates a Gaussian distribution of dynamically correlated domains. The KWW function (dotted line) clearly fails at high frequencies. Subtle, but significant, deviation from the Poisson-like distribution [frequency-dependent form of Eq. (1), dashed curve] distinguishes this liquid from a glass.

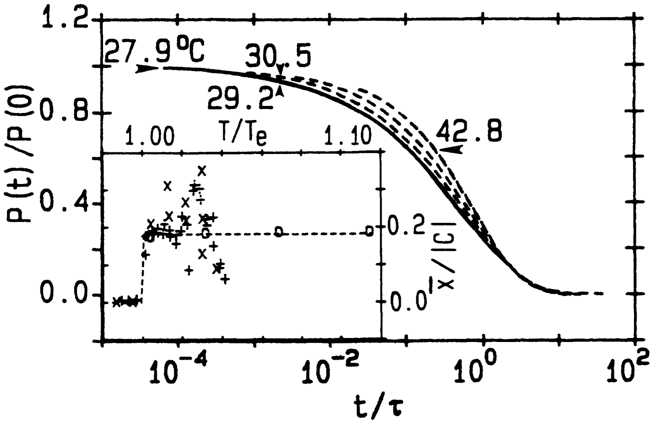

FIG. 3. Normalized stress relaxation as a function of reduced time in 60AgI-35Ag_2SO_4-5Ag_2WO_4 at several temperatures above and below $T_e=29.9$ °C. Inset: $\bar{x}/|C|$ as a function of reduced temperature from stress relaxation [using Eq. (2)] in (+) 60AgI-35Ag_2SO_4-5Ag_2WO_4 and (×) phenolphthalein, and dielectric absorption [using Eq. (3)] in (○) salol. The abrupt decrease in $\bar{x}/|C|$ at T_e signifies the transition from Gaussian distribution in the liquid, to Poisson-like distribution in the glass.

Stress relaxation in AgI-$AgPO_3$ as a function of anneal time is shown in Fig. 4. These data were obtained[24] by quenching the sample from above $T_g\approx 88$ °C to the measurement temperature 79.0 °C, then annealing for time t_A, before inducing a strain and measuring stress relaxation. There is no obvious discontinuity in the shape of the relaxation curves, but the inset reveals a sharp change in $\bar{x}/|C|$ [from Eq. (2)] as a function of t_A. For small t_A, both AgI-$AgPO_3$ and polystyrene[25] have $\bar{x}/|C|\approx 0$, consistent with the fact that Eq. (1) provides better fits to these data. After a critical anneal time (t_e), $\bar{x}/|C|$ jumps sharply back up to a value characteristic of a liquid. At a given temperature, t_e is at least an order of magnitude slower than the average relaxation time for the primary response, consistent with the very slow mixing of local relaxation rates observed with NMR.[16]

In conclusion, non-Debye response in amorphous materials is accurately characterized by a model for independently relaxing dispersive excitations on specific distributions of dynamically correlated domains. The specific distributions exist *a priori*, independent of any dynamical measurement necessary to detect their existence. Ergodic systems (liquids) possess an equilibrium (Gaussian) distribution of domains. When cooled, there is a well-defined, cooling-rate-dependent, ergodicity temperature (T_e) at which the system falls out of thermal equilibrium. Nonergodic systems (glasses) possess a locally random (Poisson-like) distribution of domains. When a glass is annealed at a temperature initially below T_e, the Poisson-like distribution exhibits a sharp transition back to the Gaussian distribution characteristic of a liquid. Careful analysis of dynamic response may be used to identify ergodicity in amorphous systems, and clarify the distinctions between liquids and glasses.

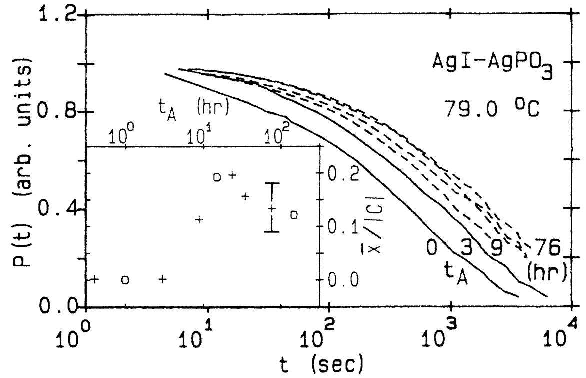

FIG. 4. Stress relaxation in AgI-AgPO$_3$ at 79.0 °C as a function of anneal time t_A (Ref. 24). Inset: $\bar{x}/|C|$ [from Eq. (2)] as a function of t_A in (+) AgI-AgPO$_3$ and (○) polystyrene (Ref. 25). The abrupt increase in $\bar{x}/|C|$ signifies the transition back to liquidlike behavior.

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